



# **A Focal Manual of Photo-Technique**

K.I. Jacobson & R.E. Jacobson





# *The Manual of Photo-Technique*

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# THE MANUALS OF PHOTO-TECHNIQUE

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# *Developing*

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THE NEGATIVE TECHNIQUE

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This book was first published in May 1940 and has been reissued seventeen times since that date. There is probably no other work on this subject that has served so many readers so long and so well as an authoritative source of reference.

Every edition preceding the Seventeenth had been brought up-to-date in the light of current progress. Yet after thirty years of wear and tear the time had come to reconsider the subject as a whole and so the last edition was reshaped to suit the prevailing trends.

Thirty years ago photographic processing was still something of a pastime which seemed to thrive on a spirit of experimentation and even controversy. The changing social structure, economics and technology of our day combine to evoke more uniform and thus more reliable concepts of developing standards and control. This is a field in which increasing automation is both desirable and feasible.

The basics of processing chemistry may not have changed a great deal, but the approach to its technology has. The range of developing agents is as wide as ever but only a few of them are consistently used in practice and optimum results are simply achieved by an informed choice of the correct formulation.

So the extensively revised Seventeenth and the present Eighteenth Edition, which has undergone further revision, present a very comprehensive survey of formulae, whenever possible in compact comparative tables. Professional and commercial practices are covered more extensively than in the preceding editions.

In this latest Edition, the Eighteenth, techniques of processing have again been revised to include rapid daylight in-cassette processing of 35 mm. film and modern tube and drum processors suitable for the professional. In the rapid access field, formulae for ultra-rapid processing are given as well as the Bimat and Dry Silver process.

Processing formulae have been brought up-to-date and wherever possible general tables of developer formulae are given. Low contrast and stabilised physical developer formulae are now included.

Reversal processing has been completely revised and so have formulae for processing of colour materials. Specific formulae are given for processing a variety of currently available colour negative and colour reversal materials.

A chapter on quality and environmental control has now been included which gives details of typical practical process control systems and control of effluents from both black and white and colour processes.

A. KRASZNA-KRAUSZ

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## *Development:*

### *What it is and what it does*

If we expose a photographic film in the camera the closest visual examination fails to disclose any perceptible change in the sensitive coating which, in general, consists of a suspension of silver bromide in gelatine and to which the name emulsion is given.

Yet we all know there has been a change and that the application of a developer will reveal it. We say that the action of the light on the sensitive material has produced a latent image. Latent here means unrevealed or undeveloped.

The development of this latent image by means of the developer is one of the most important and interesting of all photographic processes, and upon its successful operation depends in very large measure the nature of the end product, that is, the finished photograph, which is our goal.

In order to render the latent image visible we make use of certain substances known as developers, which have the property of changing the exposed silver bromide into black metallic silver. Hence we think of two processes, first a photochemical change brought about by light during exposure, second a chemical change by which the exposed silver bromide, that is the latent image, is changed or reduced to metallic silver and so rendered visible.

The chemists call this second process reduction.

If we were to introduce an unexposed film into the developer, a very small amount of silver bromide at most would be reduced to silver. Only the exposed silver bromide responds to the action of the developer and is reduced or changed to metallic silver.

It is most important to notice that those parts of the sensitive emulsion which receive most light provide the heaviest deposits of reduced silver and are therefore blackest. Where only a small quantity of light acts on the silver

bromide the amount of silver reduced is much less. If we examine the result very carefully we find that the greater the amount of light allowed to act on the sensitive material the greater the amount of reduced silver.

## THE NEGATIVE

This gives us a very interesting result: we have now got a developed picture in which all the light values of the original object photographed are reversed. The lightest parts of the original are darkest in our picture while the dark parts of the original are light in our result. That is why we call the result a negative.

This reversal of light values must always be borne in mind if we are to understand rightly the process of development and to read our negatives correctly.

We remember then that the darkest parts of the negative represents the lightest parts of the subject photographed. Therefore the highlights of our subject provide the blackest areas in our negative.

Similarly, the lighter parts of the negative represent the darker or less well-lit areas in our subject. Hence the shadows of our subject provide those areas in the negative with the lightest deposit of silver, or perhaps not even a light deposit, but clear gelatin.

## DEVELOPMENT: A REDUCTION PROCESS

We have already seen that photographic development is a reduction process in which the developer acts as a reducing agent. But photographic developers are a special kind of reducing agent, because they act only on silver bromide that has been exposed to light.

The chemist knows many reducing agents capable of reducing silver bromide to metallic silver, but they act differently to the photographic developer. They fail to discriminate between silver bromide which has been exposed to light and that which has not. A plate or film placed in such an agent would be completely blackened, irrespective of whether it had been wholly or partially exposed.

Just why the photographic developer reduces only the silver bromide that has been exposed to light is a question

we do not propose to answer in this book. Our interests are purely photographic, and a discussion of the many physico-chemical problems involved would not necessarily increase our understanding of the essentials of photographic development.

#### CHEMICAL AND PHYSICAL DEVELOPMENT

One small chemical point we must know is that in the process of reducing silver bromide to silver, soluble bromide is set free and passes into the developer solution. This is an integral part of the reduction process and is of importance because it can, under certain circumstances, cause various troubles.

In such a development process as we have described it is clear that the silver which builds up the image in the negative is derived from the sensitive film of emulsion on the plate or film, and that it is produced by the chemical reduction of the silver bromide.

We therefore call this process chemical development, to distinguish it from another process, called physical development, in which silver, already present in solution in the developer, is deposited on the latent image, a method which might be likened to silver-plating.

The composition of the developer and the method of development can naturally influence the character of the negative produced, and by suitable methods it is possible to exercise a large measure of control in the development processes. To do this with some degree of confidence we need to know something of the properties of the sensitive materials.

## *Emulsion Sensitivity and Gradation*

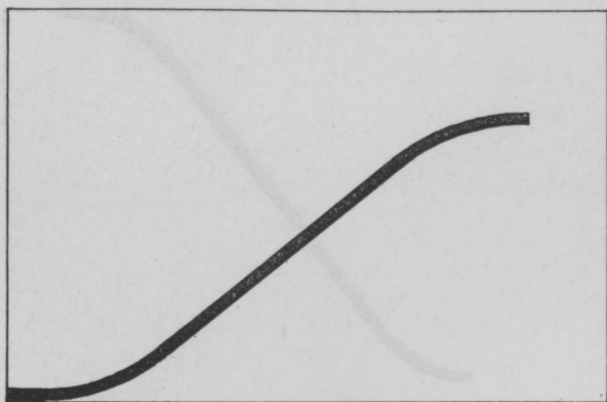
In choosing photographic material the question of sensitivity is naturally of considerable importance, but it would be a mistake to think that it was the only criterion. It would be wrong to think, for example, that the fastest, or most sensitive, film was necessarily the best. Other properties such as graininess may well play an important part and influence the final result quite as much.

On the other hand, if we have chosen the fastest and most sensitive film, then we want to feel that we know just how to develop it so that we do not lose in the processing of it just those qualities which the manufacturer has been at such pains to confer upon it.

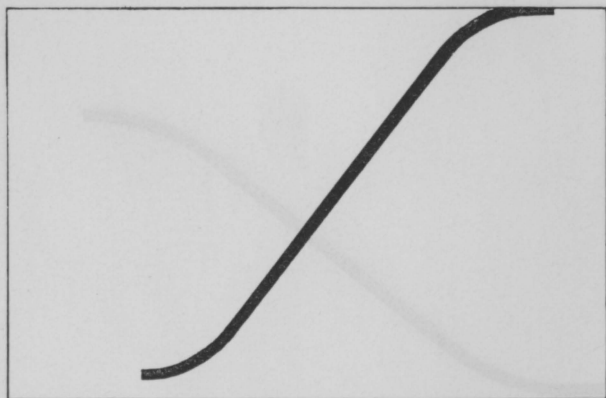
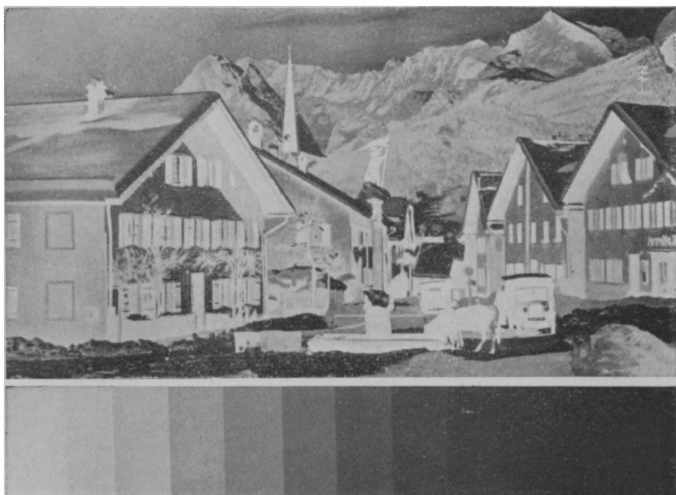
### COMPARING THE SENSITIVITY OF TWO FILMS

We may desire to compare the sensitivity of two films one with another. A quite simple experiment enables us to do this, and also to understand and investigate other properties of the sensitive material. We start from the concept that a film of high sensitivity is one requiring a small exposure to light. To put it another way, it requires only a small light impression to produce on development a given degree of blackening beyond that produced in an unexposed area, which is known as "fog".

We take two strips of the films we wish to compare and expose successive areas to a light source such that a reasonably long exposure is necessary to produce full blackening of the exposed film-strips when developed. We do this by covering up the strip with an opaque card step by step during exposure so that each successive portion of the film receives an exposure double the time of the previous exposure, for example, 1, 2, 4, 8 seconds, and so on.

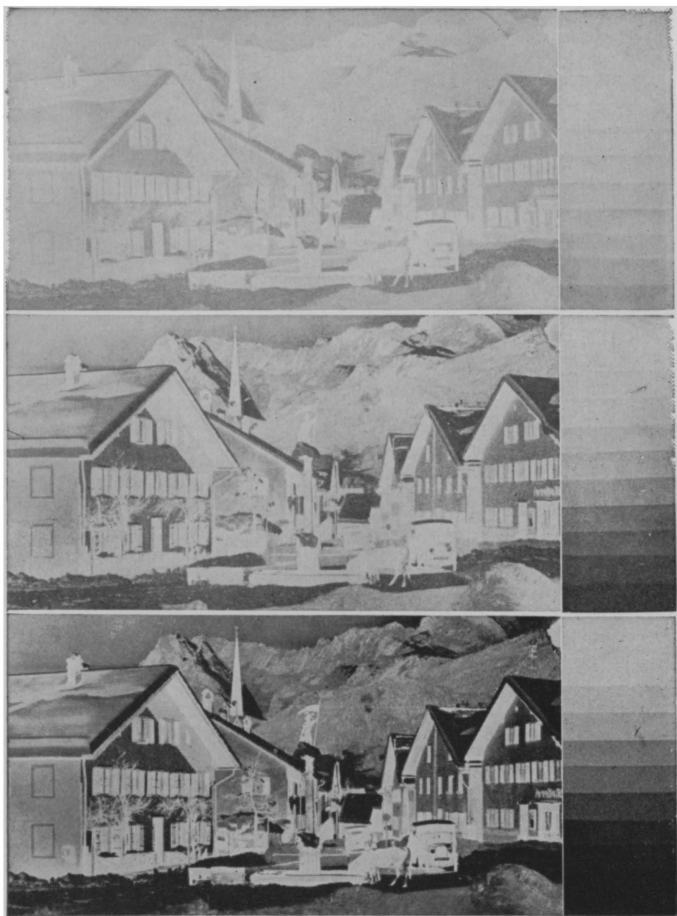


**SOFT GRADATION.** The scale of gradation is long and comprises a wide range of densities which build up the above soft negative. It will be seen that the fairly long blackening curve does not rise at a high angle, hence the gamma value (see page 34) is not high.



**HARD GRADATION.** If this negative is compared with that on page 25 it will show the difference between a soft and a hard negative. In the latter the scale of blackening is short and the curve is steeper, hence the gamma is higher. The curve also rises much higher, hence the negative has higher or greater densities particularly in the highlights.





**PROGRESS OF DEVELOPMENT IN A RAPID DEVELOPER.** In such a case the image develops so that all the details, shadows as well as highlights, appear almost at the same time (*top*). As the development proceeds, density grows all over and hence a strong and contrasty negative is seen (*centre*) until finally the required contrast is reached (*bottom*).—See page 70.



**PROGRESS OF DEVELOPMENT IN A SLOW DEVELOPER.** Here the highlights appear first (*top*), then the middle tones (*centre*) and finally the shadows (*bottom*). The negative builds up slowly from the first appearance of the high lights to the final filling up of detail in the shadows, by which time it has the necessary gradation and density.—See page 70.

When we develop these strips, we obtain what we can call blackening scales (see page 25) for the two films.

These scales will show that the two strips differ in the position occupied by the first visible trace of reduced silver. The faster film may show it at the 1-second step. In the slower film it may not appear until the step exposed for 4 seconds.

But that is not all the strips will tell us. We shall also learn that in those parts of the film which have only received a small exposure to light a certain development time is essential for full blackening. If the time of development is cut short, the effect of small exposures to light is lost and we lose some of the advantage of using a fast film.

To put this another way, if a film is under-developed shadow detail is lost (see page 27). In fact, the film which is developed for too short a time behaves as if it were much less sensitive than is actually the case. Hence we see that the time of development is of great practical importance and has a real influence on the practical sensitivity of our material. If we desire to utilise fully the whole sensitivity of our material we must develop it completely.

We can extend our experiments with strips of sensitive material by using different developers or by using developers of the same composition but of varying temperature. We shall find that all these factors are capable of influencing the result.

## MEASUREMENTS OF SENSITIVITY

Our experiments have introduced us to the rudiments of sensitivity measurements but it is important to bring out a few of the essential requirements when undertaking such sensitometric investigations. These are:

- (1) A light-source that can give a constant and controllable light output so that identical conditions of exposure can be repeated time after time. Moreover, as in the great majority of cases it is the sensitivity of materials to daylight that we are interested in, we must ensure that our light-source provides light of such colour composition, or spectral composition as it is called, that it approximates closely to daylight. Such a source is a tungsten filament, gas-filled lamp fitted

with the necessary control of electric current to maintain a constant light output.

To this must be added a filter which transmits light of almost exact daylight quality. For the photographer who desires to make only a few measurements now and again it will be sufficient to use one of the filters supplied for transforming artificial light to daylight. This filter is fixed in a frame in front of the lamp house carrying the tungsten filament lamp. This daylight filter should not be the gelatine film type, as these are liable to change in time and with use. It should be the all-glass type which is permanent and unaffected by age or use.

A light source and filter as described can be used for determining the sensitivity of any photographic material, whether ordinary, orthochromatic or panchromatic, and is particularly useful for comparing the relative sensitivity of materials in general use with new products or with materials which have not hitherto been in common use.

(2) An exposure machine or apparatus. This takes the place of the opaque cover used in simple experiments and may consist of a wedge scale of blacknesses, or, as is more usual and convenient, a step wedge in which the relation of the density or blackness of the steps to one another is known. Another method is to make use of a sector wheel which has been so cut as to provide a range of accurately determined exposures during a single revolution. For simple measurements the step wedge is recommended as being the easier to obtain and costing less than more elaborate apparatus.

Whichever type of exposure apparatus is used, the effect is to produce a graded series of exposures on the sensitive material being tested. These exposures always bear a constant relation to one another and the only factor the operator has to watch is the control of the light source. This should be arranged at such a distance from the exposure apparatus that an exposure of, say, ten seconds suffices for a very wide variety of sensitive materials. The reason for choosing an exposure of ten seconds or so is that an error of one-tenth of a second in switching the light on or off will mean only a one per cent error in exposure, whereas if the exposure time were only one second the same error would be ten per cent and therefore serious. For more accurate measurements, a

shutter must be used, producing a short exposure time in the order of the average camera exposure.

(3) Developer for the test-strips. This is of the utmost importance and calls for careful consideration, if only because the relation between sensitivity and development is the biggest factor involved in the actual technique of development. We have already seen that development can affect the result of any determination of sensitivity, for if we do not develop fully, then the sensitivity of the material being tested will appear to be lower than it really is. Hence if we are to obtain comparable results our methods of development must be most carefully controlled, so that they not only give comparable but also reproducible results. That means a developer of definite composition, used for a definite time at a definite temperature, with a well defined method of agitation. We may decide to use a reasonably energetic developer for such a time and at such a temperature that we know the strips will be fully developed. Or we can use a particular developer to attain a predetermined gradation (see page 35). Whatever method we use, it must be capable of giving identical results with identical materials as many times as we desire—and that is not the simplest thing in the world.

(4) A means whereby we can measure the degree of blackening on our developed strips. This may be some form of comparator in which the density or blackening of the developed strip is compared visually with a standard wedge of known densities and gradation. There are various types available, some of which are discussed at the end of this chapter.

In determining or measuring sensitivity, and particularly in comparisons between different materials, a most important criterion is the smallest perceptible blackening which the exposure has caused, or to put it another way, the smallest light effect which is developable on our test strip. It is particularly important that we should be able to measure this accurately, and we want also to remember that we are not dealing with the least perceptible blackening that the eye can detect; what we are considering is blackening or density which is capable of being copied when we make a print from our negative. That is the practical side of the question, and we are much more interested in a threshold value that we can reproduce in our print than in some faint deposit just

perceptible to the eye but which is without influence in reproducing a negative in positive form and is therefore outside the useful sensitivity of our material.

If we study the various methods of determining and expressing the sensitivity of photographic materials, such as the ASA, BS and DIN systems, we shall find that in the modern view it is not the first perceptible trace of light effect that counts, but the lowest density capable of reproduction when the negative is printed.

Now we must leave questions of sensitivity to discuss those other properties of photographic materials which are of importance to us in considering development and particularly the way in which they can be affected or influenced by it.

## GRADATION

Our experiment in exposing strips of film to produce a graded series of exposures provides us with a means of investigating a very important property of sensitive materials, namely gradation, and of understanding how this is related to or affected by development. In order to do this we have to consider the whole range of our strips and not merely one or two of the steps or exposures on our scale of blackening.

When we do this we can see just how any particular sensitive material reacts to a graded series of exposures, so arranged that they bear a constant ratio to one another. Such a scale of blackenings or exposures indicates what we call the gradation of any particular material, and materials can vary greatly in character as we shall see.

For example, the film on page 25 has a long range of steps between the deepest black and the lightest deposit, whereas on page 26 there are only a few steps over the same range. We call the first a soft gradation film, and the second we designate as hard. Between these two extremes there may be many different degrees of gradation and particularly that which we should call normal.

## CHARACTERISTIC CURVES

These terms soft, normal, hard, etc., have no exact significance, they are relative and only take on a quantitative

value when used in comparing properly prepared blackening curves of sensitive materials. The average photographer is rather repelled by curves and mathematical formulae, yet the expression of properties by a curve is a tremendous help in visualising clearly a collection of observations. It is infinitely easier to read and understand than are columns of figures. We have only to think of the ease of handling statistics of a recurrent character over any period of time to realise that a moment's glance at a curve can convey information which otherwise might take minutes or even hours.

So if we desire to visualise the relation between the exposure to light and the blackening it produces on sensitive material, the simplest way to do it is to produce a curve. If we wish to compare more than one material then we simply draw the curves on the same diagram.

Up the side of the diagram (see page 37) we plot units of density or blackening. The definition of density and the method of measuring it are indicated in the inset of the diagram. If we let a beam of light of intensity  $I_1$  fall on to our photographic density  $D$ , the intensity is reduced to a value  $I_2$ . We call our density one where it reduces the measuring light intensity to 1/10th, two, where it reduces to 1/100th, three, where it reduces to 1/1000th, etc. Thus on our density axis we allot equal decrements of the intensity  $I_2$  to a density unit. For example, if any two densities differ from one another by the lighter density transmitting twice as much light as the heavier one, the spacing between these two densities will be constant (and equal to 0.3) whatever the actual values of the densities may be. (For the mathematically minded it will be clear that we are defining density as the logarithm of the ratio of transmitted to incident light intensity.)

Along the base of the diagram we have divisions which represent equal increments of exposure intensity. The exposure increment axis is very similar to the density axis in that any two exposures which are in a certain ratio to one another (as for example 2 to 1) are spaced a constant distance apart on the increment axis (in this instance 0.3). (Again the mathematically minded will notice that we plot the characteristic curve on a logarithmic intensity axis.)

Now the curve itself is obtained from a series of measurements of densities which have been produced by certain exposures. On the axis described we erect verticals at

corresponding values of density and exposure; where these verticals cross we have the point of the curve. In this way we can build up and compare the blackening curves for different materials.

On pages 25-26 we have the two curves of the strips of two films that we have already spoken of, and at once we see how great a difference there is in their gradation.

In order to understand more thoroughly how to read and interpret such curves, let us consider first of all the long straight sloping portion of the curve on page 37. Here, on increasing the exposure by, for example, ten times, the amount of light transmitted by the developed density drops to one tenth since the curve rises at an angle of  $45^\circ$  to the axis; this is correct whichever exposure we start from as long as we stay on the straight-line part of the curve. In this case we speak of a correct reproduction in densities of the varying quantities of light forming these densities.

Now the actual characteristic curve is straight over only a limited range of exposures and densities. The curve bends both at the lower and the top part. With any complete characteristic curve there comes a point where increasing exposure does not increase the density. Thus at the top end of the curve is situated the region of over-exposure.

In the same way at the beginning of the curve there is a region where exposure to light causes no change in the density, followed by a region where density increases more and more rapidly with increasing unit increments of exposure—until the straight-line part is reached. The very lowest part of the curve is the region of under-exposure.

The most usual normal exposures reach from somewhere in the lower bent portion of the curve well into the straight-line portion. The region of normal or correct exposure may be said to reach from halfway up the lower bent part of the curve all the way up the straight-line part.

Looking now at the two curves on pages 25-26, we can see that there is a notable difference in their slope and therefore in the angle which their straight-line portion makes with the horizontal axis or base of the diagram. Moreover, we notice that neither curve fulfils the ideal condition of being a straight line at an angle of  $45^\circ$  to the horizontal axis and in this respect they differ from the curve on page 37. The curve of the soft gradation film makes a much smaller angle,



that of the hard gradation film a much larger angle with the axis.

### GAMMA

Gamma ( $\gamma$ ) is the tangent of the angle produced when the straight line portion of the characteristic curve is prolonged to meet the horizontal axis. It will be obvious that as the curve is steeper or less steep, so the angle will vary and so, too, the Gamma, and therefore the gradation.

Gamma, or the tangent of the angle, is measured as shown in the diagram on page 37.

In our diagram the slope of the curve is 45 degrees, hence BC and AC are identical in length and so  $BC/AC = 1$ , which is the Gamma.

If now we take the other examples, our soft and hard films on the pages 25-26, and measure them in the same way, we shall find the soft gradation film has a Gamma of 0.6 and the hard film a Gamma of 1.5.

Now that we know how we can give a numerical value to the gradation of our sensitive material, we can get on with investigating the relation between gradation and development, a matter of the utmost practical importance. For this purpose we prepare a series of strips, all with the same series of step wedge exposures and then develop them in the same developer for varying times. When this has been done and the strips fixed, washed and dried, we shall see that the development has reached a definite maximum value. If we measure the densities and plot curves for the strips we find that the steepness of gradation and also the Gamma value reach a definite maximum and then increase no more.

That really gives us two maxima, namely maximum density ( $D_{\max}$ ) and maximum Gamma ( $\gamma_{\max}$ ), or more usually Gamma infinity ( $\gamma_{\infty}$ ). The two values  $D_{\max}$  and  $\gamma_{\infty}$  just mean the maximum density and gamma that can be obtained by prolonging development.

### TIME-GAMMA CURVES

The results we have obtained with our developed strips can now be used in another valuable direction, namely in preparing a curve which clearly indicates the relation between

the length of time of development and the growth of Gamma. In other words we can prepare a time-gamma curve. To do this we arrange a diagram in which time of development appears along the horizontal axis, while on the vertical axis we have the Gamma values. As we can easily determine the Gamma from our blackening curves, so it is a simple matter to produce time-gamma curves in turn.

On page 39 curves are given for two different developers and the differences between them are apparent at a glance. The developer of curve B causes a slow increment in Gamma and the maximum reached is only low; this is a weakly active and slow-working developer. With curve A the opposite is the case, not only is the maximum Gamma reached with a comparatively short development time, but it is a high figure at that. Here we have an energetic and hence quick-working developer.

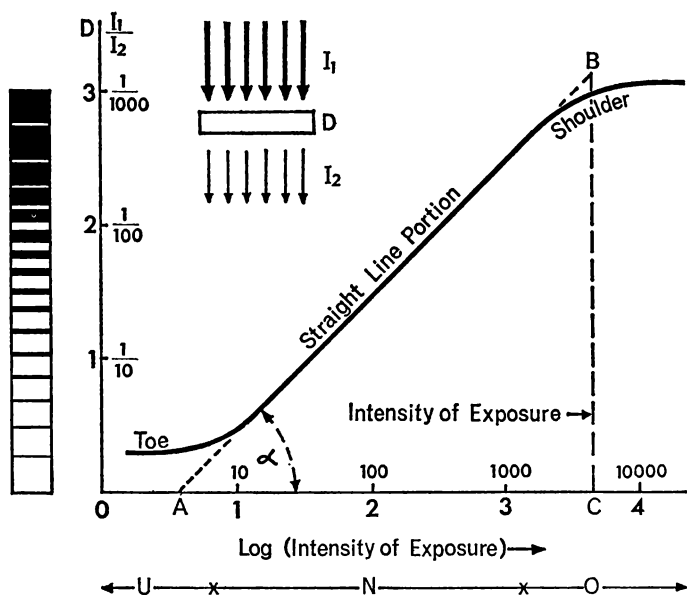
From these two examples it will be clear that in time-gamma curves we have an excellent means of characterising developers. We can see at a glance all the really important things we want to know about them, such as their relative energy as developers, the time required to reach a particular gradation or gamma and, for any particular material, the maximum gamma attainable.

In practice, time-gamma curves are not always available. Various film manufacturers supply such curves for their own material when developed with a prescribed developer. But the photographer who uses the various formulae given in this book may well ask himself what is the practical time of development for some particular film with a particular developer, not necessarily either the film or the particular developer recommended and supplied by any particular firm.

To answer this question with exactitude would require a time-gamma curve for every developer and for every film or plate sold. This is obviously impossible in view of the tremendous variety of developers and materials available. Not only is it impossible, but it is also quite unnecessary.

It is very easy to exaggerate the importance, as well as the value, of the time-gamma curve in actual practice. On the one hand we know that with a normal developer a variation of half a minute either side of full development will not seriously affect gamma, and on the other hand we know that the range of modern printing papers is so wide that we

## CHARACTERISTIC CURVE AND GAMMA.



The characteristic curve of photographic material is a plot of density against the logarithm of exposure necessary to produce that density on development. Density is defined as the logarithm of the intensity divided by the transmitted light intensity;  $D = \log I_1/I_2$ ,  $I_1$  and  $I_2$  being the intensities illustrated in the insert diagram. The values of the ratio of  $I_1/I_2$  are shown against the density values  $D$ , and similarly the exposure intensity values are shown against the log exposure in order to illustrate the logarithmic relationships. The region of under-exposure is indicated by U, that of normal exposure by N, that of over-exposure by O along the exposure axis. Gamma is a figure which expresses the contrast of a negative. It is measured or determined by extending the straight-line part of the curve until it meets the horizontal axis at A and a vertical axis erected at a point C anywhere along the exposure axis. Then gamma ( $\gamma$ ) =  $BC/AC = \tan \alpha$ . In the above example gamma is 1, for the angle  $\alpha$  is  $45^\circ$  and so AC and BC are equal.

can obtain a good print from almost any negative whether it is hard or soft.

On these grounds it is obviously unnecessary to develop a negative so that it just exactly reaches a given gamma value, for example, 0.8. What we want is a negative that is developed to such a gamma value that it will produce a good print or enlargement. That is, it should fall between the limits of gamma 0.7 and 1.0. Once the practical value of this is realised the question of the right development time can soon be dealt with in the following simple manner.

#### DETERMINATION OF DEVELOPMENT TIME

In practice, we can regard most films as falling into three groups, according to their speed rating. Group A includes slow films rated up to about 80 ASA; Group B is for medium speed films from 125-320 ASA; Group C for fast films rated faster than 320 ASA.

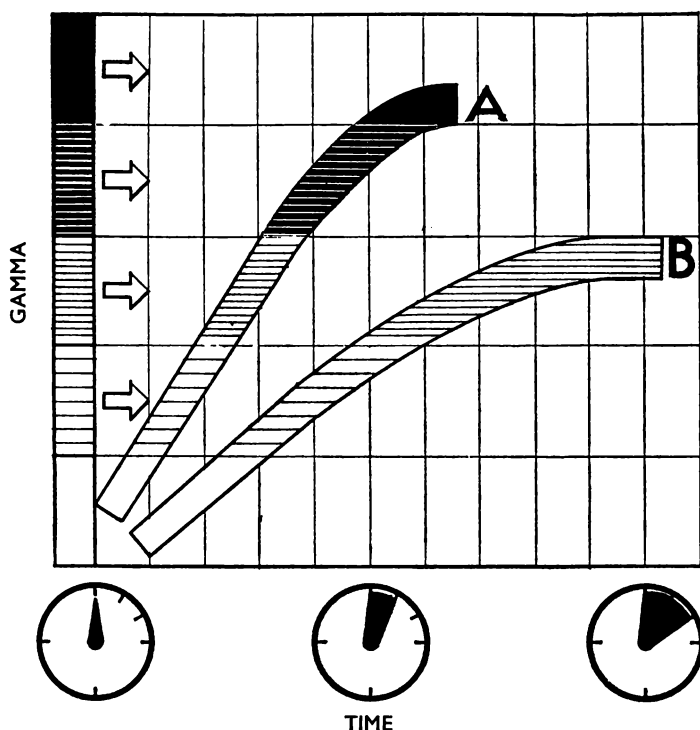
The middle group (Group B) is that which requires normal development time, i.e. the time given in the various formulae for developers. The films in the other two groups (A and C) call for either a shorter or a longer development time, i.e. a 1/3rd decrease for Group A or a one-half increase for Group C.

Example.—Suppose we choose a fine grain developer formula and that the average normal development time for this developer is 12 minutes. This will hold good for all films of Group B. If now we have a film of Group A, then the development time must be reduced to 2/3rds, that is to eight minutes. If, on the other hand, we are dealing with a film belonging to Group C, we must increase the development time by one-half, that will be 18 minutes.

The normal development times given with the various developer formulae are all chosen so that they will give a gamma of an average of 0.8 in that time, and if the above instructions relating to the three groups of films are followed then the average gamma of all negatives developed should not diverge notably from 0.8.

It is perfectly true that the rate of development may vary between films of the same group. It can even vary between films of the same grade and maker, but the divergences from the general mean which can occur in this way should be

## TIME-GAMMA CURVE



The time-gamma curve shows how the contrast of a negative increases with the development time. In order to produce such a curve, the horizontal axis of the diagram shows development time, while the vertical axis shows the Gamma values. In the diagram the effect of two types of development is shown. The curves A and B have been produced by developers with very different properties. A is a rapid-working and contrasty developer. The curve rises steeply and reaches a high Gamma value in 6 minutes. B is a slow and soft-working developer. Hence the curve rises gradually and the Gamma value is much less than that in curve A. In this case 10 minutes was required to reach even this low Gamma.

quite easily dealt with by the choice of a suitable printing paper.

#### CONTRAST INDEX

With modern emulsions and processing techniques gamma is frequently difficult to measure because of the unusual curve shapes obtained. Also many exposures are made in the toe region of the characteristic curve. These difficulties have led to the definition and use of the term Contrast Index and similar concepts. Contrast Index is the Kodak term, defined in their Data Sheet SE-1A as *the slope of a straight line joining two points on the characteristic curve that represent the approximate minimum and maximum densities used in practice*. Development of different films to a given gamma generally affords negatives that are best printed on different grades of paper. Development of different films to the same CI value, however, gives negatives that yield acceptable prints on the same grade of paper.

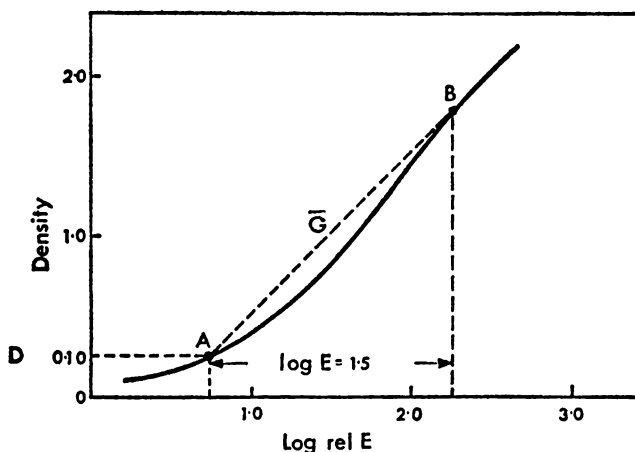
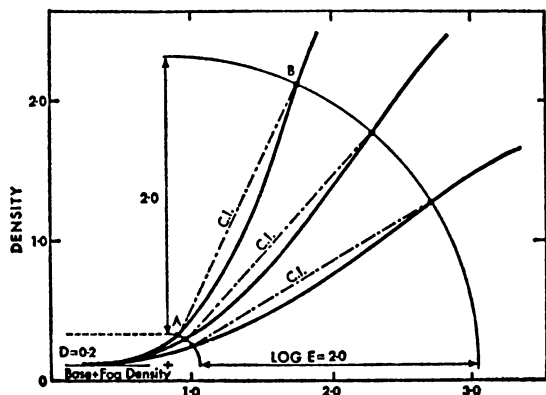
To determine the CI two arcs are drawn from a common point on the base+fog axis. The intersection of the smaller arc of radius 0.2 density (or log exposure) units with the characteristic curve gives the low-density point (A). The intersection of the larger arc of radius 2.2 density (or log exposure) units with the characteristic curve gives the high-density point (B). The slope of the line joining the points A and B is the Contrast Index (page 41). For easy measurement of the Contrast Index Kodak recommend the use of a transparent template.

#### AVERAGE GRADIENT ( $\bar{G}$ , "GEE BAR")

Ilford have adopted the criterion of average gradient ( $\bar{G}$ , "gee bar") as a measure of contrast in place of gamma. This is slightly easier to measure than contrast index and both give similar variations with development time although their absolute values are slightly different. At the present time there is, unfortunately, no universally accepted alternative to gamma as a measure of contrast and both contrast index and average gradient are commonly used. Kodak express development data for their products in terms of contrast index whereas Ilford use average gradient.

In order to measure average gradient a point A is located

## CHARACTERISTIC CURVES: CONTRAST INDEX AND AVERAGE GRADIENT



*Top:* The slope of the line between the points A and B gives the contrast index (CI). Points A and B are obtained from the intersection of arcs of radii 0.2 and 2.2 density units, drawn from a common point on the base + fog axis, with the characteristic curve.

*Bottom:* The slope of the line between the points A and B gives the average gradient (G). Point A is 0.1 density units above base + fog density and point B is 1.5 log exposure units to the right of A.

on the characteristic curve 0.1 density units above the fog level and a point B is located on the curve 1.5 log exposure units to the right of point A. The slope of the line joining points A and B is the average gradient (page 41).

## DENSITOMETERS

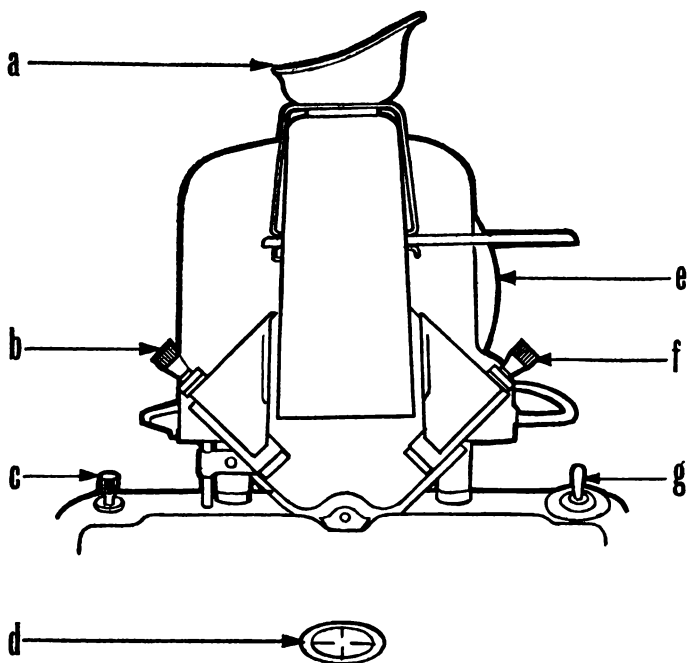
The densitometer is an important accessory and is useful in a number of different ways for testing photographic materials and for the control of processing generally. To plot the characteristic curves discussed in a previous chapter, a densitometer is required to measure the density of the photographic materials. Density measurements may, on the face of it, appear to be very simple and all that is necessary is to take an exposed and processed sample, place it in a light beam and measure how much of the incident light is transmitted. However, things are not quite so simple, as the silver deposit is in the form of relatively large particles which do not only scatter the light, but also absorb it. Some of the incident light will also be lost by reflection on the surface of the sample.

### “DIFFUSE DENSITY”

Depending on how measurement is made, a multiplicity of numerical values of density may be obtained for a given sample. “Specular density” is obtained when the illumination on the sample is direct and only the directly transmitted light is included. “Diffuse density” is measured when the illumination is direct and all the transmitted light is included in the measurement or when the illumination on the sample is diffused and only directly transmitted light is included in the measurement. “Double diffuse densities” are obtained when the illumination is diffused and all the transmitted light is measured. The ratio of the specular to the diffused density is known as the “Callier Co-efficient” and is related to the graininess of the material and the conditions of exposure and development. The type of density closely related to most conditions of photographic practice is the “*diffuse density*” as defined in the British Standard No. 1384/1947.



## OPTICAL REFLECTION-TRANSMISSION DENSITOMETER



Densitometric control is of great assistance in producing negatives and prints of consistently high quality. A simple but accurate instrument for this purpose is the optical reflection-transmission densitometer. The drawing shows the Kodak instrument of this type which makes reading the densities of negatives, transparencies and prints a straightforward job. Its versatility is based on a dual lighting system whereby densities are measured visually by either transmitted or reflected light. The parts are (a) eye piece, (b) reflection zeroing screw, (c) transmission zeroing knob, (d) optical disc, (e) scale wheel filter holder, (f) reflection zeroing screw, (g) reflection transmission switch.

## VISUAL DENSITOMETERS

To measure the diffuse density of photographic materials, two main types of densitometer are available, visual and photo-electric instruments. In visual densitometers, two beams of light are brought together in a circular field and when the illumination of both beams is the same, the field is of uniform brightness. When the density to be measured is inserted in one of the beams, that portion of the field will get darker and to restore both portions to the same illumination, the comparison beam has to be reduced by a known amount. In most visual densitometers in use today, the intensity of the comparison beam is compared by a neutral wedge.

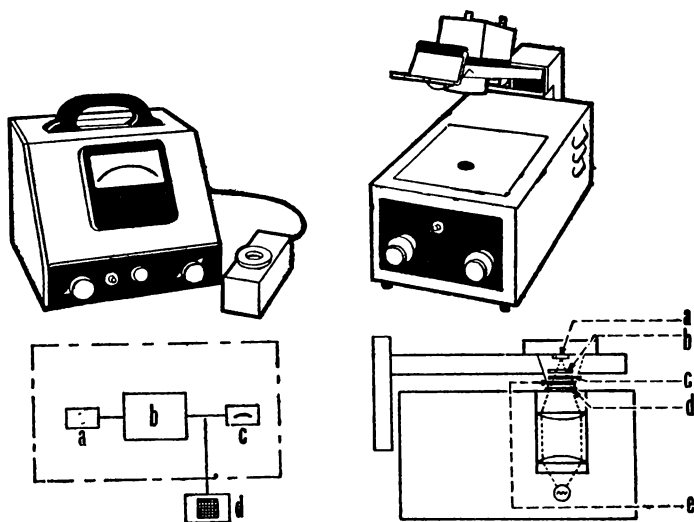
An instrument of this type is the Kodak reflection-transmission densitometer. For transmission densities the light is provided by a lamp mounted in the base below a flashed opal disc. Another lamp mounted immediately behind the rotatable annular wedge in the measuring head provides the comparison field. Two lamps, fitted at the lower end of the measuring head provide the illumination for measurement by reflected light. The annular density wedge itself is made of methyl methacrylate and contains a carbon pigment. Its construction ensures a uniformly linear density scale and a high degree of stability.

Before measurement, the zero setting is first adjusted so that the two fields seen in the eyepiece are in balance, i.e. the outer and inner fields match in brightness. The sample to be measured is then placed over the opal disc with the area to be measured inside the guide lines. The light source in the base illuminates the sample which is seen through a small aperture in a mirror. This sample field appears in the centre of the finder lens. The comparison light source projects the beam through the wedge and collecting lens via the mirror, to the finder lens, thus giving the comparison field. The density is measured by rotating the wedge until the outer comparison field again matches the inner sample field in brightness.

## PHOTO-ELECTRIC DENSITOMETERS

Photo-electric instruments are more convenient and rapid in use. They use vacuum photocells or selenium cells. The Baldwin densitometer belongs to the first group. It consists of

## VACUUM-CELL DENSITOMETER



Using vacuum photo-cells, the Baldwin Densitometer consists of two main units, the photometer and the density unit. The photometer (*left*) consists of (a) photocell, (b) amplifier, (c) meter, (d) recorder (optional). The transmission density unit (*right*) contains (a) photocell, (b) shutter, (c) filter, (d) sample to be measured, (e) diffuser.

two main units, the photometer and the density unit. The photometer, which houses the amplifier, has two controls besides the on/off switch. One of these selects the density range to be used while the other adjusts the zero setting. The mirror scale is calibrated to show densities between 0 and 1.0, and there is no compression of the scale at the upper densities.

The range selector switch is marked 0, +1, and +2 and in the last position densities up to 3.0 can be read. Owing to the sensitivity of the photocell used in this instrument, densities as high as 6.0 can be measured accurately by placing neutral density filters of known value in the filter holder prior to zeroing the instrument. The high sensitivity of the densitometer makes it useful for colour work as well: there is no difficulty in reading colour densities through filters.

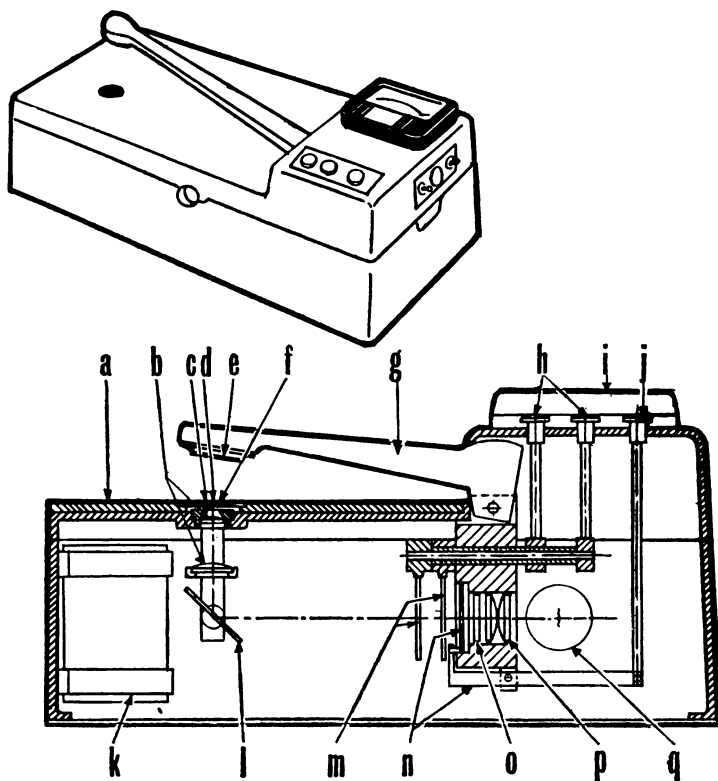
The other unit is the transmission densitometer which is so designed that measurements can be made at any distance up to 12 in. from the nearest edge of the negative or transparency being measured. A sliding filter holder with four openings is available for colour work. Two aperture plates are provided with the densitometer allowing readings to be taken of densities in areas 1/16 in. and 3/16 in. in diameter.

Instead of the transmission unit, a reflection density unit can be used for the measurement of the density of positive prints in colour or black and white. It measures the light reflected from a small spot about 1 in. diameter which is illuminated by a light beam at an angle of 45 deg. The light is reflected perpendicular to the illuminated surface before entering the photocell. Provision is made for the insertion of colour filters. The density range of the reflection densitometer is 0 to 3.0 accurate to within 0.02, and 3.0 to 4.0 with a slightly lower accuracy.

An instrument based on the use of selenium cells is the Eel Universal densitometer which is available in two models, the Minor for surfaces up to 12 in. wide and the Major for surfaces up to 24 in. wide. There are three apertures available: 1 mm., 2 mm. and 4 mm. diameter. To avoid errors in reading the higher densities on the logarithmic scale two range control buttons are located on the front panel. In this way densities from 0 to 3 can be easily read. A layout of the Eel Densitometer is shown on page 47.

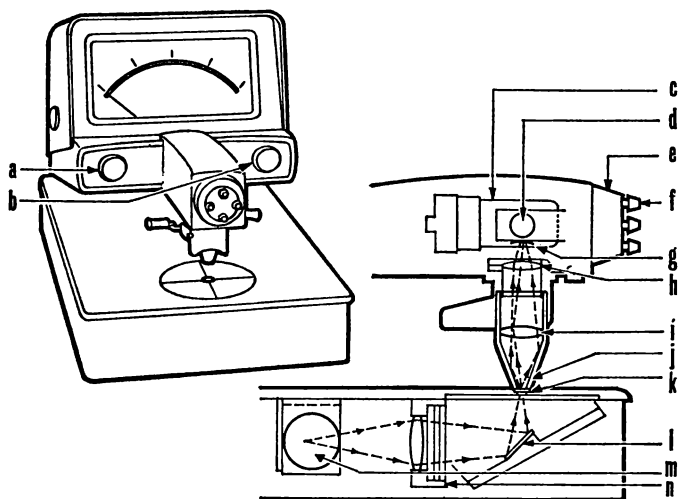
The reflection head is available as a plug-in accessory to

## SELENIUM-CELL DENSITOMETER



The Eel universal densitometer is based on the use of selenium cells. A standard 12-volt, 36-watt automobile-type lamp (q) is supplied from a stabilising transformer (k). The light beam passes through a condenser lens (p), heat absorbing glass filter (o), an iris control for zero setting (n), and two gauges each of density 1.0 (m). The beam is then deflected by an angled mirror (l) to another lens system (b) to focus on the aperture (f). The light passes through the sample (d) and falls on a barrier layer photocell (e) mounted at the end of the moveable friction loaded arm (g). The current generated by the photocell is fed directly into a microammeter (i), having an inverse logarithmic scale for direct readings of optical density. The two gauges (m), each of density 1.0, are controlled by two push buttons (h). The iris control is operated by the knob (j).

## PHOTOMULTIPLIER TUBE DENSITOMETER



The Macbeth Quantalog Densitometer TD-102 uses a photomultiplier tube (c). A 6.3 volt, 4.0 amp tungsten bulb (m) is powered from a stabilised source. After passing through a lens, dichroic filter and heat absorber (n) and deflection by a mirror (l) the light beam is focused on the aperture disc. (k) The sample is placed between the aperture disc (k) and the diffuser (j). The light beam is then focused on the photomultiplier tube cathode (g) by the lenses (i and h). The appropriate filter (d) may be selected by rotating the filter selector (e).

Calibration of the instrument is accomplished by the use of a calibrated step wedge by adjustment of the zero adjust control (a) and the calibration control (b) so that the scale reads the correct density values.

the Universal Densitometer. A neutral filter of density 1.0 is normally in the light beam within the instrument and after adjusting the iris to obtain zero reading on a white surface, reflection densities up to 1.0 are read directly from the meter. For higher densities, the neutral filter may be swung aside when the meter indicates densities between 1.0 and 2.0.

Another instrument used for the rapid determination of transmission densities is the Macbeth Quantalog densitometer model TD-102 which uses a photomultiplier tube as the detector. This instrument has a filter turret assembly for use in colour as well as black and white measurements. Densities within the range 0-4.0 and 0-6.0 density units may be measured for colour and black and white respectively. In addition to calibration of the instrument by adjusting the calibration control after zeroing the instrument by the zero adjust and using a calibrated step wedge, the calibration reference control may be used. This is an internal reference filter which may be interposed in the optical system simply by moving a lever. For colour measurements the instrument is calibrated as before but when the colour filters are placed in the light beam the filter trim controls are adjusted so that the instrument gives the required reading.

## *Image Structure*

We have learned something of the way in which the characteristic curve can throw light on development processes in general (see page 33). Now let us follow the process of development somewhat more minutely, especially as it proceeds in the actual emulsion and affects the structure of the developed image.

If we examine an average negative with the naked eye it appears to consist of a homogeneous deposit of black silver with quite as regular a texture as a layer of black pigment. If, however, we use a fairly strong lens, we shall see that the silver deposit consists of numerous grains of quite varied and irregular structure.

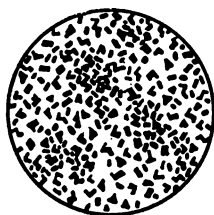
In enlargements from the negative this irregularity sometimes attracts attention in an unexpected and often unpleasant fashion. This is graininess and it is caused by the granularity of the negative image. It is the reason why one of the most important problems in photography is the reduction of the grain size of emulsions and the use of the correct development technique.

### **GRAIN AND DEVELOPMENT**

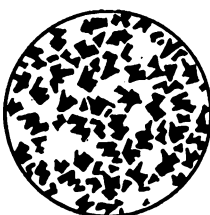
Let us take a step further in our investigation of grain and granularity and call to our aid a microscope giving us a much greater magnification. First, let us glance at an undeveloped emulsion (page 53). We can see the individual grains of silver bromide and we note that they show crystalline form. What happens to these grains during development? Fortunately it is not necessary for us to carry through an extended investigation to answer this question. That has been done by many workers using photomicrography and cinematography and their results are at our disposal. From them



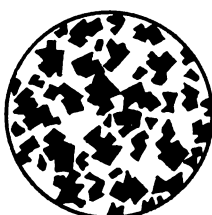
## GRAIN AND GRANULARITY



50 ASA



125 ASA



320 ASA

If we examine an average negative with the naked eye it appears to consist of a homogeneous deposit of black silver, with quite as regular a texture as a layer of black pigment. If, however, we use a fairly strong lens, we shall see that the silver deposit consists of numerous grains of quite varied and irregular form. The larger the individual silver grains in an emulsion, the more sensitive it is. A film of 320 ASA is enormously more grainy than one of 50 ASA, while a film of 125 ASA is mid-way between the two. In an enlargement from the negative, this irregular structure might become obtrusive and unpleasant. That is graininess, caused by the granularity of the negative image. It emphasises the need to choose the film and development technique most suited to the result required.

we know that the actual process of development does not begin equally over the whole surface of one of the grains: it starts from some particular point on the grain. This occurs on many grains simultaneously and gradually each grain is reduced to black metallic silver. Where two or more grains touch one another the whole mass tends to be reduced to a clump of silver whose form bears no resemblance to the original grains. Generally the developed silver grains have a very irregular character and are much larger than the original grain of the emulsion.

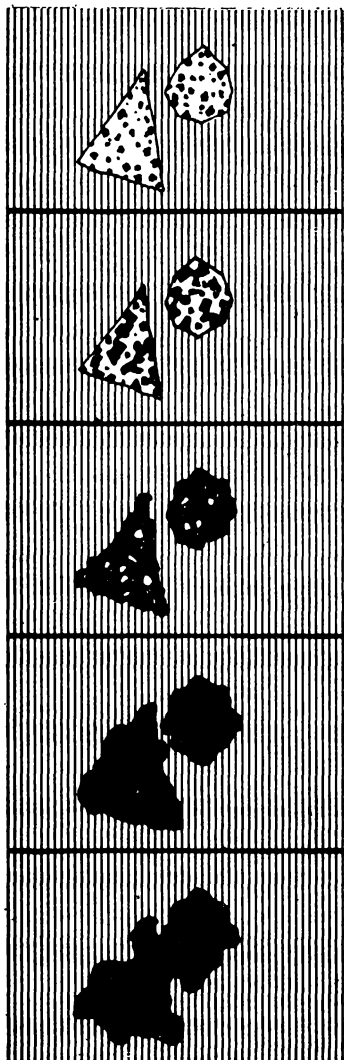
Page 53 illustrates various stages in the process of development. We see grains in which development has just begun, others in which it has advanced some distance and yet others where development is complete and the whole grain has been reduced to metallic silver.

Both the character and the size of the silver grains can be, and are, enormously influenced by the development process. For example, by developing for a short time, we can obtain a very fine-grained silver deposit, but only by sacrificing all that full development can give us, and particularly the advantage of the full sensitivity of our material.

The granularity of negatives is naturally a function of the properties of the emulsion itself and the photographic manufacturer exercises all his ingenuity and care to ensure that his emulsions shall be as fine-grained as possible. Nor do his efforts cease with the attainment of small single grain size. He equally takes every possible precaution against any clumping together of the grains in the emulsion.

The graininess which so often mars an enlargement is not due to the size of single grains, for these are far too small to cause such an effect. It is caused by apparent clumping together of the grains. In a photographic film there may be up to 40 or 50 grains in layers on top of one another. Developed photographic deposits thus appear irregular; there seem to be large masses of grains which produce comparatively large masses of reduced silver in the negative. The mere touching of grains in the emulsion can help to this end, for, as we have seen in our study of the development process, a developable grain in contact with another which has received no exposure usually means that both are developed.

## THE SILVER BROMIDE GRAIN



This diagrammatic representation of two emulsion grains at a very high magnification shows that development begins at definite centres on the grain (*top*). These centres grow and soon the original form of the grain is altered by the appearance of reduced silver, which alters the outward form of the grain. As the development proceeds, it is seen that the reduced silver in the two adjacent grains bridges the gap between them and so forms one large, irregular grain of developed silver (*bottom*). The effect of a fine-grain developer is to develop the single grains and to obviate the clumping together of adjacent grains.

## GRANULARITY AND GRAININESS

The terms "granularity" and "graininess", as used in the preceding paragraph have very definite meanings, although they are often misused.

Granularity refers to the grainy structure of the photographic silver image itself and can be evaluated in measurable terms. Graininess is the inhomogeneity we see as a result of granularity, i.e. the visual subjective appearance of this pattern. The graininess produced by a material of a certain granularity varies with the conditions under which we look at the result.

The cause of the granularity of the negative has already been considered. The grainy structure—granularity—is responsible for the visible effect of graininess in the print, which becomes worse at greater degrees of enlargement.

The subjective impression of graininess depends also on the viewing distance and is less noticeable as the distance increases. In practical photographic terminology we use granularity mainly in connection with the negative while graininess refers mainly to the print. These terms have a different meaning although they are often used in the same sense.

## NEGATIVE GRANULARITY

The granularity of the negative depends on:

- (1) *the negative emulsion*. The granularity of an emulsion increases with an increase in speed. High-speed emulsions have a high granularity and the graininess becomes noticeable at enlargements of 8-10 diameters. Medium-speed emulsions can be enlarged by more than 10 diameters without producing an objectionable degree of graininess.
- (2) *the exposure*. The negative density should be kept low as higher density leads to an increase in granularity. The exposure should therefore be as short as it is consistent with good tone reproduction.
- (3) *the developer*. The correct choice of developer is of primary importance, as is explained on pages 64-66.
- (4) *the conditions of processing*. To achieve the optimum result with the chosen developer, time and temperature must

be controlled carefully. These conditions have to be adjusted in such a way that the correct gamma is obtained (page 38).

## PRINT GRAININESS

The graininess of the print is influenced by the following factors:

- (a) The type of enlarger.
- (b) The contrast and the surface structure of the paper.
- (c) The conditions of viewing the print.

Contrast in enlarging increases graininess. If the same negative is enlarged on two papers with different degrees of contrast, the print on the more contrasty paper shows more graininess. This does not provide an easy method of controlling graininess because the choice of paper is determined by the contrast of the negative. We choose the paper that gives the best possible relationship between the tone reproduction of the print and that of the original scene. Graininess in the print can, however, be somewhat suppressed by the choice of a paper with a matt or, still more, a grained surface.

In a similar manner, the condenser-type enlarger enhances contrast and leads to more noticeable grain than a diffused ("softer") light source. Any measure which reduces the sharpness or contrast of the print, such as the use of soft-focus lenses or similar devices will, of course, reduce graininess too.

Graininess is much less obvious if the enlargement is viewed from a distance. The grain may therefore be less noticeable in very big enlargements which can be viewed from comparatively large distances.

## RESOLVING POWER

The grain size of the film emulsion effects the quality of the print not only because graininess depends on it, but also because it controls the image resolution. Fineness of grain results in smoothness of tone in the picture and also affects its fineness of detail. This ability of the emulsion to record fine details is its *resolving power*.

The resolving power is measured by photographing on a reduced scale a test object consisting of sets of lines of

decreasing size separated by spaces having a width equal to the width of the lines. The photographic test is examined under magnification to determine the finest set of lines which can be individually distinguished. The numerical value of resolving power is the number of lines per millimeter.

Resolving power depends mainly on the grain size of the emulsion and to a lesser degree on the type of the developer. A high-energy developer, while producing maximum speed, leads to greater granularity than one of lower activity. To obtain minimum graininess the first rule is to choose the finest-grain film that has sufficient speed for the purpose in question.

The fineness of the silver grain is, however, not the only factor determining the visual quality of the picture. Often, an image which appears sharper than another is actually much coarser in grain.

## IRRADIATION

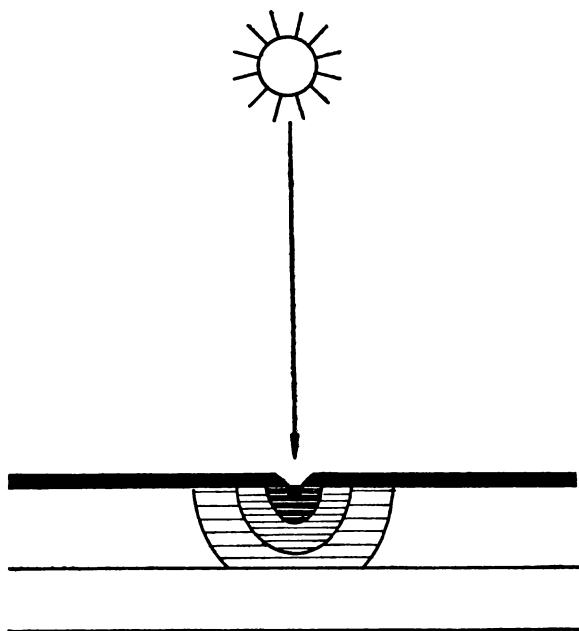
To understand the difference between the effects of these two factors (grain size and developer energy) on the image quality, we must give a little attention to another phenomenon which takes place in the emulsion. We must investigate the way in which a beam of light acts and how it progresses as it passes into the photographic layer.

The photographic emulsion is what the physicist calls a turbid medium and one of the notable properties of turbid media is their power of scattering light. Hence, when a beam of light falls on a photographic emulsion it does not pass directly through it as would happen with a transparent medium. It is scattered and so may reach areas which are not subject to direct illumination.

This is illustrated on page 57 where we have a highly magnified section of a film, protected by an opaque mask which allows a very fine ray of light to pass through a tiny aperture. This ray of light is scattered by the turbid medium, the emulsion, and so spreads laterally, thus affecting areas which are actually protected from direct light by the mask.

It is quite easy to see that if the mask had two tiny apertures close together, each allowing a tiny beam of light to fall on the emulsion, the lateral spread or scatter of the light in the emulsion would result not in two points affected

## IRRADIATION



The photographic emulsion is a turbid medium and therefore has the property of scattering light, a process which can seriously affect the sharpness of the image. The diagram shows a highly-magnified section of an emulsion which has been covered by a sheet of metal with a small aperture through which a beam of light falls on to the emulsion. With a very short exposure, only the point where the light meets the emulsion will be developed. But if the exposure is longer, the light is scattered so that it spreads beyond the area protected by the metal, and hence irradiation takes place, although the area affected by the scattered light is actually protected by the metal cover.

by light, but in one diffuse area much larger in extent than either of the points due to the direct action of light on the film. It is obvious that this scattering of light will affect the image quality and interfere with its sharpness.

#### HALATION

If we follow the track of light further through the emulsion and into its support, we shall see that when it meets the film-base/air inter-face at a particular angle, it is reflected back into the film and can reach the emulsion again, thus producing halation. Various methods of reducing halation are shown on page 61. A light absorbing filter layer is coated either on the back of the film base or—better—between the emulsion and its support. Another method consists in dying the film base itself. By these means halation can be restricted but never completely eliminated.

#### IMAGE SHARPNESS

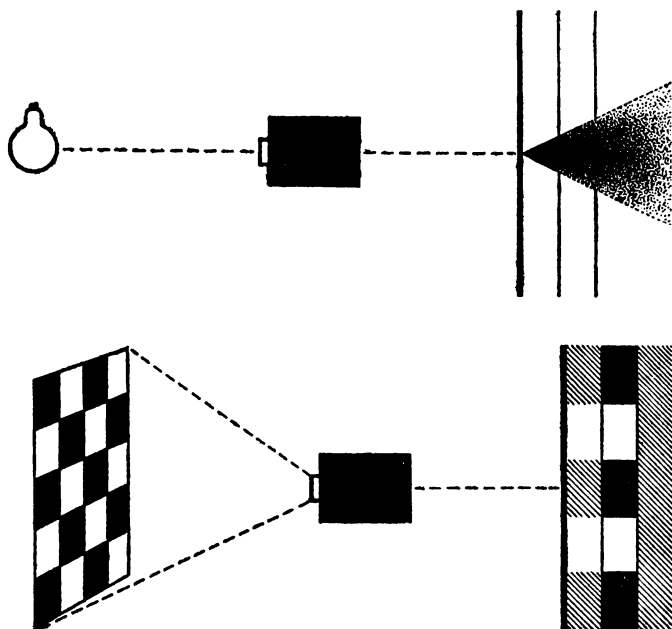
These two phenomena of irradiation and halation, in addition to the grainy structure of the emulsion, can have a very adverse effect on the quality of the image. They cause blurring of the image and the sharpness of line suffers. The change in density along the line of separation between a light area and a dark area is not sufficiently abrupt and sharp to produce a crisp image. It is the degree of abruptness of the change in density along the hard line of separation between a light and a dark area that determines the “sharpness of definition” or “image sharpness”.

The physical measurement of image sharpness, in this sense, is called acutance. It is a measure of the abruptness of the change in density along the line of separation between a light and dark area. The steeper the transition, the higher the acutance. The ability to obtain negatives of high acutance, capable of producing pictures of the best possible sharpness, depends in the first place on the properties of the film (see page 63).

When the bulk of camera work involved mainly contact printing or low degree enlargements from negatives of fair size, the interests of the majority of camera users were considered to be best served by films having the maximum



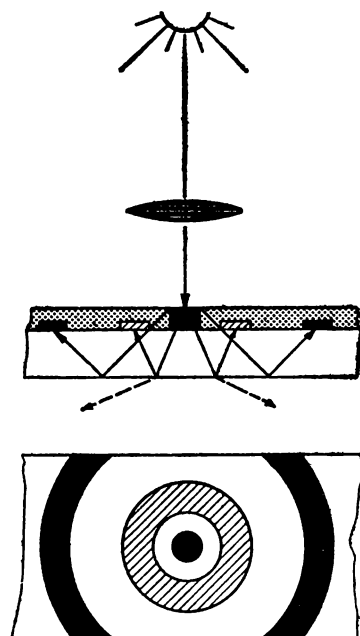
## EMULSION THICKNESS



*Top:* A ray of light which enters the emulsion of the film is scattered inside, so that a sharply-defined point is not formed in the negative. Instead, a dark circle is formed round the central black dot, which becomes less and less dense towards its edge. The "definition" of a film is thus greater when its emulsion is thin than when it is thick.

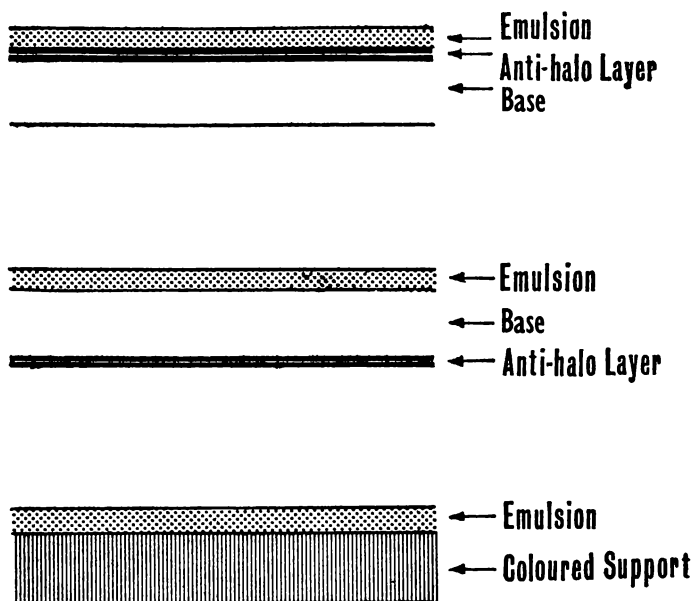
*Bottom:* Increasing the exposure latitude of a film by using a double-coated emulsion. The lower emulsion is less sensitive than the upper one, and if a flat image appears in the top one because it is given excessive exposure, the lower emulsion is affected and adds density where the single top emulsion would have lost it.

## ORIGIN OF HALATION



When a beam of light of sufficient strength falls on the emulsion, it not only passes through the emulsion but also through the film support. When it reaches the film-air boundary, it will be reflected back to a greater or lesser extent, depending on the angle at which it meets the boundary surface. In this way, it again reaches the emulsion on the under side and so produces a developable spot or halation. In the diagram, two forms of reflection are shown. In the case of the light falling at a steep angle, part of it is not reflected back and the part which is reflected is therefore of comparatively low intensity. The light which falls at a wider angle suffers almost complete reflection and hence the effect is much more marked.

## PREVENTION OF HALATION



In the diagram, three methods are shown whereby halation can be prevented. First, by the introduction of an anti-halo layer between the emulsion and the support. Secondly, by the coating of the back of the film with an anti-halo layer. This absorbs any light which passes through the emulsion and prevents it being reflected back. Third, halation is prevented by coating the emulsion on a coloured support. This method is used largely with films for miniature cameras.

exposure latitude. This led to the introduction of double-coated roll films capable of recording a wide range of exposures.

These films consist of a highly sensitive upper coating which rests directly upon a much less sensitive emulsion. The combined action of these two emulsions confers a wide latitude in exposure to the film. In cases of overexposure, for example, which would normally produce a flat, inferior negative, the lower and less sensitive emulsion takes over to increase the total range and so ensure a printable negative (see page 59).

From the point of view of image sharpness, however, such films are far from ideal. The thick, double coating is particularly susceptible to scattering of light and the image is more or less blurred. Where only contact copies or small enlargements are required, this may not be a matter of great importance. The lack of definition is, in fact, hardly noticeable. But for greater enlargements the double-coated film or indeed any thick-coated film is totally unsuitable.

As modern camera technique prefers the use of small negatives requiring high degrees of enlargement, the question of good exposure latitude must take second place to good definition. Thinner coatings of higher turbidity offer less opportunity for scatter within the emulsion and the image sharpness is consequently increased. These films, with a single thin coating, have a comparatively limited exposure latitude, but this is no problem for the modern photographer with an automatic camera or a reliable exposure meter at his disposal.

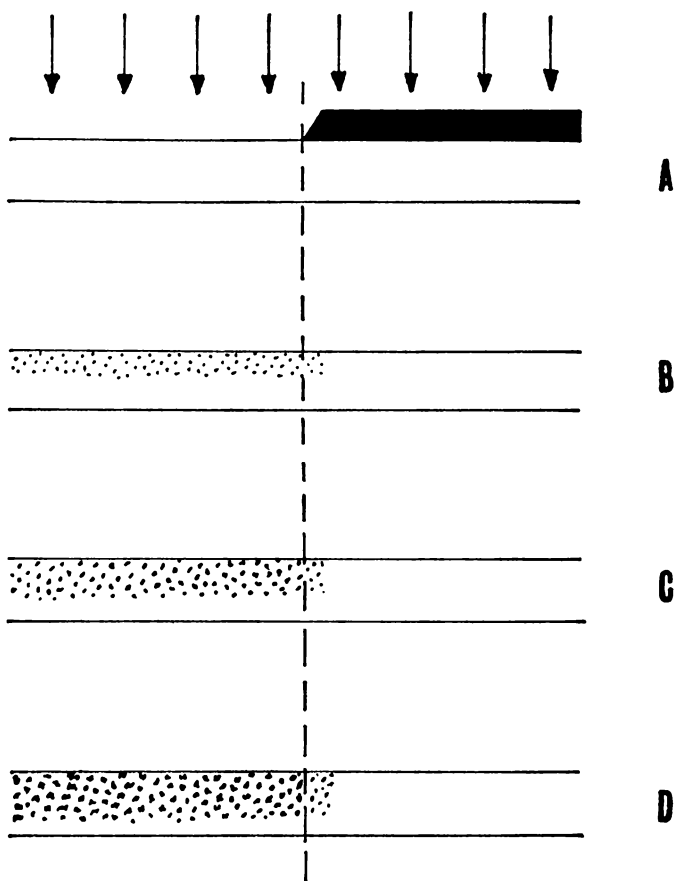
#### MODULATION TRANSFER CHARACTERISTICS

Modulation transfer characteristics indicate the effects on the microstructure of the image caused by diffusion of light within the emulsion. The results can also be modified to a certain extent by development effects.

The term "modulation transfer" has been introduced by Kodak Research Laboratories in place of what has been variously called "sine-wave response", "contrast transmission function" etc., in accordance with recommendations made by the International Commission for Optics.

In obtaining these data, patterns having a sinusoidal variation in illuminance in one direction are exposed on to the

## ACUTANCE OF EMULSIONS



A highly magnified section of a film exposed while part of its surface is protected by a knife edge (A). With increasing exposures the light is scattered and may reach areas which were not subjected to direct illumination (B, C and D).

film (see page 65). After development, the photographic image is scanned in a microdensitometer, the densities of the trace are interpreted in terms of exposure, and the effective modulation of the image is calculated. The modulation transfer is the ratio of the modulation of the developed image to the modulation of the exposing pattern. The modulation transfer curves show a plot of this ratio as a function of the spatial frequency of the patterns in cycles per millimeter. By multiplication of ordinates of the individual curves, the modulation transfer data for a film can be combined with similar data for the optical system with which it will be used, to predict the final image-detail characteristics.

In the illustration, page 65, the bottom panel is the sinusoidal test object, the next panel the photographic image magnified to the size of the original test object, and above that the microdensitometer trace of the image. After the characteristics of the lens have been taken out, a plot of the effective exposure of the film alone is shown in the curve, i.e. the effective distribution of light in the test object. This is the modulation transfer response of the film alone. Usually the scale of frequencies is either linear or logarithmic, but in the illustration it is arranged so as to correspond to the frequency of the original test object.

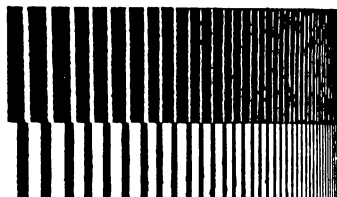
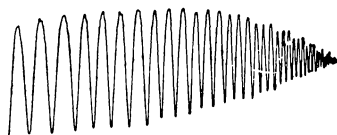
Two typical modulation transfer curves are shown on page 65, one representing a high speed negative film, the other a low speed positive film. The right-hand graph in each case is on an arithmetic scale, while the left-hand graph is on the logarithmic scale. The latter-type curve not only has theoretical advantages, but is also easier to use when curves must be combined with technical data for other components of a system for study and evaluation of the overall performance characteristics.

#### THE CHOICE OF FILM AND DEVELOPER

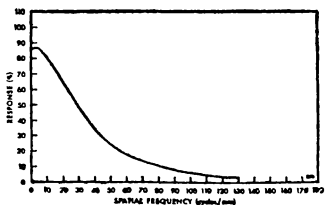
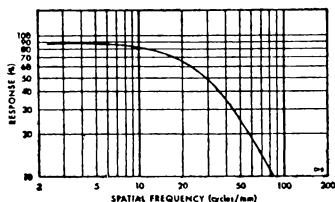
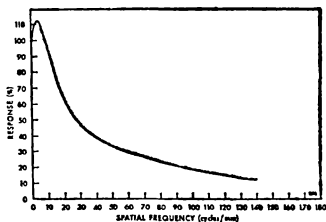
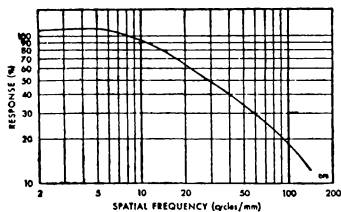
The modern high-acutance films are not only inherently capable of giving improved image sharpness, but they also lend themselves to a special processing technique which artificially enhances image sharpness. This method involves the use of so called "high definition" developers (see page 214) which take advantage of the edge-effects described on page 77. This results in the production of a much harder

# MODULATION TRANSFER CHARACTERISTICS

(Right, bottom): The sinusoidal test object and the photographic image magnified to the size of the original test object. (Right, centre): The microdensitometer trace of the image. (Right, top): A plot of the effective exposure of the film, i.e. effective distribution of light in the test object.



(Below): Typical modulation transfer curves representing in the upper pair a high-speed negative film and in the lower pair a low-speed positive film. In each case, the left-hand graph is on a logarithmic scale, the right-hand on an arithmetic scale.



and more abrupt change of density across the line between light and dark areas, which gives the impression of much increased sharpness. The term *acutance* is applied to a rather complicated mathematical measurement of the rate of change of density across this edge (see page 216).

Wherever circumstances allow it, it is clearly best to choose a high-acutance film to be processed in a high-definition developer. A limitation to the use of these thin-coated films, however, is their comparatively slow speed.

In general the choice of a negative developer is governed in the first place by the size of the negative in question, apart from cases where the nature of the negative material itself requires special developers. For sizes larger than  $2\frac{1}{4} \times 3\frac{1}{4}$  in. any type of standard negative developer is likely to prove entirely suitable. For roll films, the first choice will usually be a standard fine-grain developer (Table XXXI). For miniature films there is the choice between fine-grain, super fine-grain and high-definition developers as we shall see later (page 202).

In all cases, for the best results the degree of development of the negative must be adjusted to the characteristics of the printing (or enlarging) equipment and material. Basically it is best, from the points of view of print quality and working convenience, to adopt a technique by which the majority of average negatives print best on to medium-contrast paper under normal conditions of enlarging. Expressed in gamma values (page 35) this means that sheet films should be developed to a gamma of approximately 0.8, while a somewhat lower gamma—0.6 to 0.7—is generally adopted for roll and miniature films.

## OPTIMUM EXPOSURE

Every photographer should be aware of the fact that his success depends in the first place on the correct exposure of the film in the camera. First, however, let us define what we mean by the term "correct exposure".

In the early days of photography, the aim was for all the tones of the negative to lie in the straight-line portion of the gradation curve (page 37). This is useful insofar as the negative then renders the various brightness areas of the scene in their true ratio of values. But this does not necessarily mean



that the same is true for the print, because we also have to take into consideration the curve of the paper which is by nature much shorter than that of the negative. This deficiency in the tone rendering properties of the paper can be compensated for to some extent by the deviation of the negative curve from the straight-line form. To achieve this, the camera exposure must be kept on the short side so that the shadow values of the scene fall on the "toe" of the gradation curve (page 37).

The old rule that it is better to over-expose than to under-expose, still stands in cases of emergency when the photographer is in doubt about the correct exposure. To make sure of a printable result it is certainly better to choose an ample exposure rather than a too short one. But this does not mean that over-exposure is advisable as a general rule. On the contrary, for the reasons explained above it is the modern practice to reduce camera exposure to the minimum consistent with good rendering of shadow details.

#### QUALITY OF THE NEGATIVE

Finally let us summarise the main factors on which negative quality depends:

- (1) Tone gradation.
- (2) Fineness of grain.
- (3) Sharpness of definition (acutance).

(1) *Tone gradation.* From the practical point of view, it is desirable that the tone gradation of the negative allows the choice of a paper of medium contrast. To produce such negatives is mainly a question of correct development, a suitable developer at the right developing time. By adequate exposure we have made sure that the shadow details of the subject will be rendered in the negative, provided of course that this is not spoiled by under-development. Likewise we have to make sure that the high-light areas in the negative are printable. For the visual assessment of the negative we can use the following procedure: If the negative is held close to a printed sheet in good light, the letterpress should just be readable through the densest parts of the negative.

To produce negatives of good printable quality, the gamma (page 35) of the characteristic curve should be kept

within 0.7-0.9 by controlling the developing time. This range of gamma permits, too, quite a good exposure latitude.

For special purposes, such as press or industrial photography, negatives of a gamma between 0.9 and 1.2 are often preferred. The exposures must then be more accurate to avoid the production of negatives which are very dense and therefore rather inconvenient to print.

Correct exposure and correct development will lead to a negative of good tone reproduction. There is however, another factor that might seriously interfere with the result, namely the non-image forming glare light. This can arise from several sources, such as light scattered or reflected by the glass-air surfaces of the lens system, by flare in the glass of the lens and by dust or finger prints on the lens surfaces. Light can also be reflected from the lens mount, the iris and the shutter blades. Flare light can reduce the tone scale considerably because it has a much greater effect on the shadows than on the highlights. While a certain amount of flare light is inevitable, it should be kept to the minimum by cleaning the lens and by using a lens hood.

(2) *Fineness of grain*. Granularity is primarily a property of the film emulsion and is largely determined by its speed. However, we have already seen that the development has a certain effect on the quality of the negative in this respect, too. To obtain a negative of low granularity, exposure should be kept to the minimum and a fine grain developer should be used.

The finer the grain of the emulsion, and the better it is preserved by correct negative technique, the higher the image resolution (page 55), i.e. the ability of the film to record fine details. Even under these conditions a kind of graininess can be obtained which is in fact due to microreticulation caused by unsatisfactory control of the temperature of the processing solutions. It is therefore important to control not only the temperature of the processing solutions themselves carefully, but—under extreme conditions—even the temperature of the wash-water.

(3) *Sharpness of definition (acutance)*. The quality of the image does not depend only on the fineness of the grain. Indeed, it has been found that an image which appeared sharper than another was in fact considerably coarser in grain. We have therefore to deal with two different factors: the fine-

ness of the grain determines the resolution i.e. the rendering of fine details, whereas the sharpness of the contours of the objects of the scene depends on the acutance of the negative.

Assuming the optical system can produce a sharp image, the degree of sharpness actually obtained depends on certain properties of the photographic emulsion and on the processing technique. We have already dealt with the emulsion. So, where good definition is of primary importance, a high-acutance film should be chosen, i.e. film with a thinly coated emulsion of high turbidity (page 62).

The image sharpness can further be enhanced by the choice of a high-definition developer. These developers make use of the adjacency effects (page 214) and we shall have to deal with their formulation and application later on.

## *The Progress of Development*

It might be expected that in the case of thinly-coated emulsions the process of development would take place through the whole film simultaneously; this is, in fact, rarely the case. Development almost invariably commences at the surface exposed to the developer and only slowly progresses into the interior of the emulsion (see page 71).

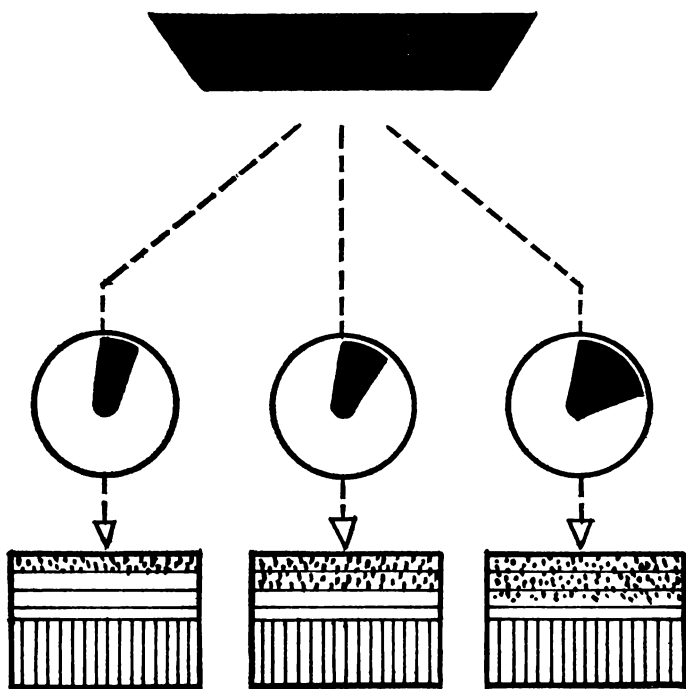
This is partly dependent upon the fact that the gelatine of the emulsion layer must swell in order to permit the developer to diffuse into it. Also as the developer acts on the silver bromide it naturally is used up or exhausted and development can only progress if the used-up developer is replaced by fresh solution. Naturally, the exposed silver bromide is not distributed evenly throughout the film.

### THE RATE OF DEVELOPMENT

The manner in which the developer acts and the speed with which it penetrates the emulsion layer is largely dependent on the nature of the developer. Later on we shall discuss the differences between surface and depth developers in some detail.

One factor which plays an important part is the energy of the developer; an energetic developer produces a heavy density at the surface of a film before it has had time to penetrate to any depth, whereas a less energetic or slow-working developer will produce an equal density only when it has had time enough to penetrate into the emulsion and to develop the deeper layers. This difference is shown diagrammatically on page 73. Both films have the same density to transmitted light, but the distribution of the developed grains is different, those in the film developed with

## PROGRESS OF DEVELOPMENT IN THE FILM



The clock faces show the passages of time during development and the sections show how development proceeds. We see that development begins at the surface of the film and progresses downwards into the thickness of the film. This method of progress is dependent upon various factors. First, the gelatine must swell to permit the diffusion of the developer. Next, as the developer is used up in development, it is essential that there should be a free flow or diffusion of the developer in order that action may take place in the deeper layers of the film. Hence while progress at the surface is rapid, later on more time is required for the developer to penetrate and act on the inner portion of the emulsion.

the weak developer being much more widely and deeply distributed than is the case in the film treated with the energetic developer.

#### THE INFLUENCE OF TEMPERATURE

As is the case with most chemical reactions, and photographic development is a chemical reaction, the rate of development depends upon temperature. The higher the temperature of the developer the more rapid and energetic will be the progress of development. This rule holds good for all developer substances but the actual degree of acceleration for a given rise of temperature varies with the different developers.

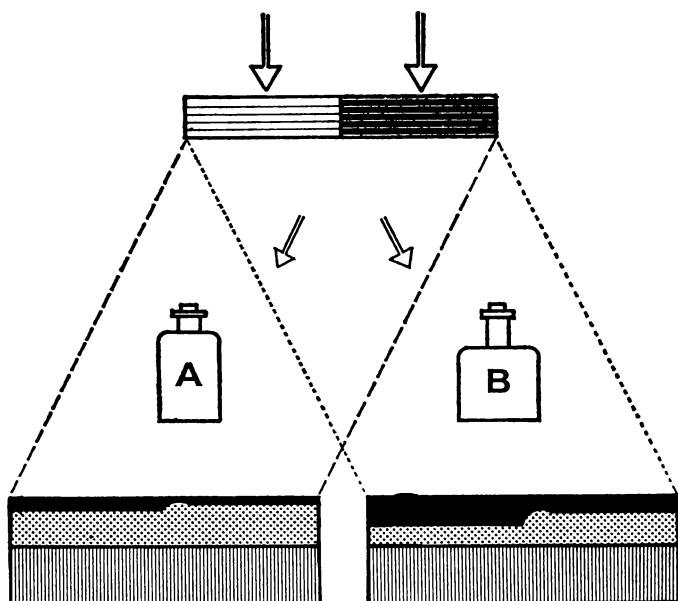
The increase in speed of development with an increase of 10°F. is taken as the Temperature Coefficient of the developer. For example if we find that a particular developer works twice as quickly at 75°F. as it did at 65°F. then we say that it has a Temperature Coefficient of 2. The following table gives a rough guide to the time-temperature relationship of the three main types of developer, assuming Temperature Coefficient of 1.8 for standard MQ developers, 1.6 for fine-grain and 2.3 for super fine grain developers.

I.—TIME-TEMPERATURE TABLE FOR STANDARD DEVELOPER GROUPS

°F.	°C.	M.Q. Min.	Fine Grain Min.	Super Fine Grain Min.
55	13	10	19	50
60	15	8	15	35
65	18	6	12	25
68	20	5	10	20
70	21	4½	9	15
75	24	3½	7	12
80	27	2½	5½	8
Temperature Coefficient		1.8	1.6	2.3

The Temperature Coefficient is not solely influenced by the developer substance; the formula, and in particular the

## RAPID AND SLOW DEVELOPMENT



The diagram shows two plates, each of which has been given a long exposure on one half and a short exposure on the other half. In the case shown on the left the negative has had a rapid development, that on the right a slow development. But in both cases overall blackening has resulted. The energetic developer A has caused a strong blackening on the surface of the film, while the slower developer has attained a like blackening, but has required much more time. The developer A gives a strong surface image, while developer B has given rise to an image which is much deeper in the film, although both pictures appear to have the same contrast when examined by transmitted light.

quantity and type of alkali present, plays a part. Thus, each developer has its own Temperature Coefficient. Nevertheless, for most practical purposes, this can be taken as 2. That means that development time should be halved for each 10°F. (6°C.) rise in temperature.

A development temperature of 20°C. (68°F.) is usually considered as normal, but there is a trend towards using a higher temperature (24°C., 75°F.) as it is easier to warm a solution than to cool it.

For convenience most manufacturers publish charts for their particular films and developers from which it is possible to read the appropriate development times for various temperatures. A typical time-temperature chart for the development of negative materials is illustrated on page 75. In order to estimate the development time at a temperature other than 20°C. (68°F.) the diagonal line from the recommended time at 20°C. is followed until it cuts the horizontal line representing the actual temperature to be used. The new development time at this temperature is then read from the bottom line of the chart vertically below the intersection. Thus if the recommended development time is 8 minutes at 20°C. (68°F.), at 24°C. (75°F.) the required development time will be 5½ minutes and at 18°C. (65°F.) it will be 10 minutes.

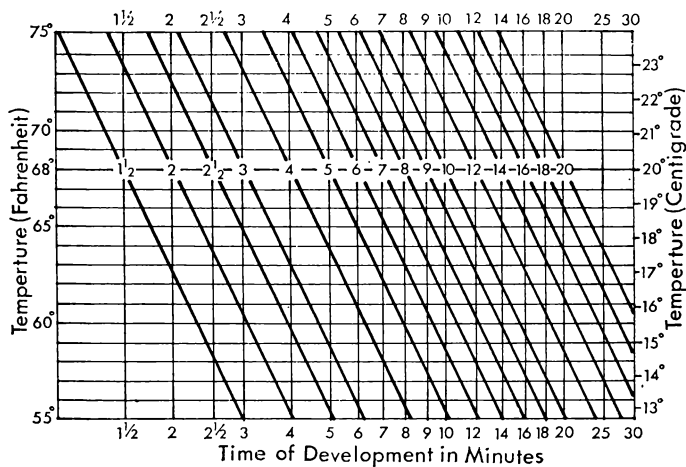
#### WHEN IS THE DEVELOPER EXHAUSTED?

This very practical question is difficult to answer by any simple and generally applicable formula, because the useful life of any developer depends upon a whole series of factors not easily assessable.

Of these the most important is the quantity of negative material which a given volume of developer solution will develop. It is also important to consider whether all the developing will be done in one big operation or, on the other hand, if intervals of time will occur between one batch of developing and another. The class of material developed will also play a part, the thickness and the type of emulsion, its content of stabilising constituents and the extent to which they will retard the development process. Another factor is the amount of surface of the developer exposed to the influence of atmospheric oxidation and the time of such exposure.



## TIME-TEMPERATURE CHART



A typical time-temperature development chart published by Ilford Ltd from which it is possible to read development times at temperatures other than 20°C. (68°F.).

Finally it must not be overlooked that it is not the total area of film that is to be thought of as contributing to the exhaustion of the developer but only that part which has actually undergone development.

For all these various reasons any direct or comprehensive answer to our question is not easy. For the majority of developers in use today, details will be found in the directions for use which will indicate the quantity of material developable by unit quantity of developer and will also usually say what extra time of development should be allowed after a certain number of films have been developed. In some cases the necessary replenisher is given and this is a matter that should receive the attention of all careful and economical workers.

Table II gives approximate figures for the keeping properties and useful capacities of various developers in common use.

## II.—KEEPING PROPERTIES AND USEFUL CAPACITY OF DEVELOPERS

	*Stock solution in full bottles	Working Solution		**Sheets 8" × 10" per 1 gallon (4.5 litres)
		Dish	Tank	
D76, DK20	6 months	24 hours	1 month	30
D23, D25	6 months	24 hours	1 month	20
D11, D50, D93, ID11, ID36, ID62, ID68, D60a	6 months	24 hours	1 month	40
D19, ID19, ID72	6 months	24 hours	1 month	60-80

\*Partially-filled bottles one-third of full-bottle life.

\*\*Approximate equivalents: 1 rollfilm 120; 2 rollfilms 127; 1 35 mm. film (36 exposures); 1½ sheets 6½ × 8½ in. or 18 × 25 cm.; 2½ sheets 4½ × 6½ in. or 13 × 18 cm. 4 sheets 4 × 5 in.; 6 sheets 3½ × 4½ or 9 × 12 cm.

## DEVELOPER REPLENISHERS

The decrease in developer activity with use can be overcome up to a degree by increasing the development time. The better procedure and the only one when large quantities of solutions are involved is to compensate for developer exhaustion by adding small quantities of replenisher solutions at intervals as required. These replenishers are usually of such strength

that when used to replace the developer carried out on the film, the developer activity is kept approximately constant.

The quantity of developer carried out with the film varies, of course, according to the processing conditions. If after replenishment the developer is still below normal activity some of the old developer must be discarded and more replenisher added. If, on the other hand, the developer tends to gain strength from replenishment the replenisher should be diluted with water (say, two parts replenisher with one part of water). The diluted solution is then added to maintain the working solutions at the required level.

Small volumes of developers are best replenished by the addition of a definite quantity of replenisher for each roll or sheet film processed. Usually the developer activity will be satisfactorily maintained by adding the indicated quantity of replenisher for each 500 cm<sup>2</sup> of film.

This is equivalent to:

- 1 sheet 8 in.  $\times$  10 in. (20.3  $\times$  25.4 cm.)
- or 4 sheets 4 in.  $\times$  5 in. (10.2  $\times$  12.7 cm.)
- or 1 roll film 120 (620)
- or 1 35 mm. film of 36 exposures

The following procedure is recommended. After processing, for instance, one roll film, pour the indicated quantity (usually 20–30 ml.) of replenisher solution into the empty developer storage bottle. Then return enough used developer to the bottle to bring it up to the original volume, discarding any excess. If the original volume is not reached add unused developer solution or replenisher diluted two parts with one part of water.

It is naturally inadvisable to exhaust and replenish a developer indefinitely because the solution accumulates a lot of foreign matter such as particles of gelatin, silver sludge etc. The developing solution should be examined carefully and discarded when its condition makes it advisable. Developed films should also be inspected carefully in order to find out whether they show any indication of the developer giving trouble such as variation of contrast and density, stain, and fog, etc. Test strips can be used for this purpose.

#### DEVELOPMENT EFFECTS

Some development effects are phenomena of only scientific interest and we shall not deal with them here. Others have

an important bearing on the course of development and even on the quality of the result.

These phenomena can best be demonstrated by giving one half of a film a strong exposure, the other half only a weak exposure. The sharpness of the boundary between the two areas of different density suffer not only from the emulsion effects of "irradiation" and "halation" (pages 56, 58) but also from adjacency effects in development. In the area of low exposure the developer has little work to do. So, relatively fresh developer passes to the area of intense exposure and assists its development just across the border line, where it produces a small region of increased density. This phenomenon is called the *border effect*.

On the other hand, reaction products from the development of the heavily exposed area diffuse into the lightly exposed part and retard its development near the boundary. This creates a region of lower density than that of the remainder of the lightly exposed area. This phenomenon is referred to as the *fringe effect*. The two lines so created have also been called *Mackie lines*.

A microdensitometer curve showing the variation in density across the line between the two areas has the appearance shown on page 216. The two edge effects are represented by the increase in the density on one side of the border and by the depression in density on the other side.

A special form of the border effect is the *Eberhard effect*. Between two small areas of different size, but equal exposure, the smaller area will in general have the higher density. Again the reason is the action of the non-exhausted developer which is available for this area.

As we shall see in the next chapter, these development effects can cause trouble. We shall, however, also learn that controlled use of these developing effects can actually improve the quality of the negative. It is worth mentioning that Phenidone developers give much weaker edge effects than MQ developers.

#### THE INFLUENCE OF AGITATION

It is self-evident that agitation of the developer can have a considerable influence on the development effects described in the preceding paragraphs.

Let us consider first an extreme case in which the solution is completely undisturbed and suffers no agitation whatever. In such a case the areas close to highlights will be occupied by increasing quantities of exhausted and bromide-rich developer and as a result the development will be slowed down.

In the shadow area of the negative the developer will naturally be only slightly affected because only small amounts of silver bromide have to be reduced; therefore development proceeds unaffected. This means that in the highlights development is restrained and the contrast of the negative is diminished. In addition, markings of varying density may be developed which, as we shall see later, (page 394) can produce serious faults.

Next, let us consider a case in which the negative or the developer solution has hardly been stirred, certainly not sufficiently to move the exhausted developer away from the surface of the negative quickly. That means that the major part of the developing has to be done by this exhausted developer and that entails a greater or lesser degree of retardation of the development. This emphasises the fact that the agitation of the developer is no matter of insignificant influence on the speed of the development but is of particular importance as regards the time of development and the contrast of the negative.

Hence we should ensure by good agitation of the developer that the exhausted solution is replaced by fresh developer as quickly as possible and that throughout the process the developer is maintained in a well-mixed condition. This does not necessarily mean constant agitation, although steady movement is advisable.

As an example of the effect of agitation on the progress of development, it may be taken that where intermittent agitation is used about 50% longer development time should be given than would be considered necessary with constant movement.

# *The Composition of the Developer*

A developer consists of many different chemicals, mainly:

- (1) The developer substance,
- (2) The preservative,
- (3) The alkali (or accelerator),
- (4) An agent which restricts fog formation or slows the action of the developer as a whole.

The nature of the chemicals, as well as the relative quantities present, govern the properties of the developer to so great an extent that it is important to understand exactly the role of each constituent.

While it is correct to say that the most important constituent of any developer is the developing agent itself, it does not appear correct to commence a description of a developer with the actual developing agent for the simple reason that it is the *composition* of the solution that plays the dominant part in determining the photographic properties of the developer. We know, for example, that many developing agents can provide slow acting and weak, or rapid and contrasty developers according to the composition of the solution and the relative amounts of preservative and alkali present. The photographic behaviour of the developing agent is therefore less a function of the substance itself than of the total composition of the developing solution. Hence it appears logical to deal first with the other constituents and to explain their effect on the developer substance.

## THE PRESERVATIVE

Development, as we have already seen (page 22) is a reduction process, in which silver bromide is reduced to silver and the developer substance itself undergoes a change, being oxidised.

It has to be noted, however, that the development process itself is not necessary for the oxidation of the developer. Mere exposure to the oxygen of the atmosphere will quickly oxidise the developer and render it useless. To prevent this oxidation taking place, or at least to reduce its rate, a preservative is added to the developer and the most widely used substance for this purpose is sodium sulphite.

### *Sodium Sulphite*

Sodium sulphite plays an important part in the developing process itself. The oxidation products of the developing agents, formed during the reduction of the silver halide, have an undesirable effect on the developing process. Some of these products can accelerate the developing process, while others have a retarding effect. Both effects are undesirable because they make control of development considerably more difficult.

Furthermore, most of the oxidation products decompose to usually coloured compounds which stain the gelatine of the emulsion. In certain cases use is made of this effect by the controlled addition of a limited amount of sulphite to the developer. The stained oxidation products are then formed in situ with the dyed image which can be useful to increase the printing density of the negative.

By adding a sufficient quantity of sulphite, the formation of these products can be almost completely prevented. In the case of hydroquinone for example, its oxidation product quinone combines with sulphite to produce a sulphonate. This is a colourless, water-soluble product which has practically no effect on the course of development.

Another important property of sulphite is its solvent action for silver halide. It can therefore have a noticeable influence on the graininess of the silver image. This action of the sulphite will have to be considered in greater detail in the chapter on fine grain developers.

Sodium sulphite comes in two forms, as a crystallised salt and as an anhydrous powder. The crystalline form is more commonly used, but the anhydrous salt is to be preferred. One part by weight of the anhydrous salt is the equivalent of two parts by weight of the crystalline. In all other respects the two salts are similar in their action.

The anhydrous salt is often preferred because of its better keeping qualities; the crystallised salt tends to change in the air and the decomposition gives rise to sodium sulphate which does not act as a preservative in developers. Another advantage of the anhydrous salt is that it dissolves quickly and easily.

Generally speaking the purity of the anhydrous sodium sulphite on the market leaves nothing to be desired. This is of particular importance in compounding fine-grain developers which often contain a high proportion of sulphite and in which the sulphite plays quite an important role other than that of preservative.

As, however, the principal object of adding sulphite to a developer is to guard against the oxidation of the developer substance by the oxygen of the air, it is naturally important to adopt a definite sequence of operations in compounding a developer and in general the order of addition of the components to the solution should be:

1. Sulphite.
2. Developer substance.
3. Alkali.

This order should not be varied unless special instructions are given with any formula for some other order to be followed.

### *Bisulphites*

It is sometimes advantageous to replace sulphite by bisulphite, and the salt most generally used for this purpose is either potassium or sodium metabisulphite.

There is an important difference between sulphites and bisulphites in that solutions of sulphites are weakly alkaline whereas solutions of bisulphites are distinctly acid. This difference materially affects the properties as well as the applications of the two salts.

Developing agents or substances, with certain special exceptions, are only active in alkaline solution, hence when bisulphites are used there must be sufficient alkali present in any normal developer to neutralise the free acid and convert the bisulphite into sulphite. In practically all published formulae it will be seen that the proportion of alkali present is ample for this purpose, the only exceptions to this rule being special developers such as those based on amidol



and certain of the fine grain and physical developers which will be discussed later in this book (pages 202 and 218).

Potassium metabisulphite is sometimes objected to on account of expense and sodium bisulphite suggested as a substitute. The sodium bisulphite of commerce is mainly sodium metabisulphite and not the sodium hydrogen sulphite which comprises true sodium bisulphite. This is no disadvantage to the photographer and he can at all times replace potassium metabisulphite by an equal weight of the sodium salt, as the properties of the two materials are practically identical.

Another form in which bisulphite is sometimes recommended, especially in Europe, is bisulphite lye, which consists of a concentrated solution of sodium bisulphite containing about 10 oz. of solid bisulphite in 32 oz. of solution. (It has a specific gravity of 1.32 at 60°F. and is designated as 35° Baume.) It is but little used by photographers either of Britain or the United States. One hundred parts by weight of potassium metabisulphite are equal to 205 parts by volume in bisulphite lye, i.e., 10 oz. by weight metabisulphite = 20½ fluid oz. of lye.

The amounts of the alkalies commonly used in photography which neutralise unit quantities of potassium metabisulphite are given in the following table by L. P. Clerc.

### III.—EQUIVALENT QUANTITIES OF ALKALIES

<i>To neutralise 100 parts by weight of potassium metabisulphite take</i>	Of sodium carbonate anhydrous	95 parts
	„ sodium carbonate crystal	258 „
	„ potassium carbonate dry	124 „
	„ sodium hydroxide (caustic soda)	36 „
	„ potassium hydroxide (caustic potash)	50½ „

### *Sulphite or Bisulphite?*

We have seen that the addition of alkali to a bisulphite converts it into a sulphite. Why, then, should we use a bisulphite in preference to sulphite?

In the first case, it is fairly common to make up developers in two solutions, one of which contains the developing substance and the sulphite, and the other the alkali. In such a

case bisulphite should replace sulphite because with its acidity it inhibits oxidation, and thus solutions will keep much better. Quite unnecessarily some formulae still use sulphite in such a case: they are given in this book in the form in which they are published.

Next there is a decided advantage in using bisulphite in more than usually concentrated solutions of developer, owing to the greater solubility of the bisulphites.

Another point which must not be overlooked is that in the case of a one-solution developer in which sodium sulphite and bisulphite occur with sodium carbonate, the sodium bisulphite neutralises an equivalent amount of sodium carbonate in accordance with the following reaction: Sodium bisulphite + sodium carbonate = sodium sulphite + sodium bicarbonate. In this way the proportion of alkali is reduced, an apparent restraining action is exerted and the life of the developer is prolonged because some of the alkali has been destroyed.

In addition to its action as a preservative, sulphite has another valuable property which is made use of in development processes. When silver bromide is in a finely divided condition, sulphite has a certain amount of solvent action on it and so is made use of in certain fine-grain developers which act in part as chemical but also in part as physical developers as will be seen when we come to discuss these processes.

#### THE ALKALI (OR ACCELERATOR)

Solutions of developer containing only sulphite have, as a rule, only very weak developing powers, and may, indeed, show none at all. In order to develop their full action, the addition of alkali is necessary.

The alkalies most widely used in photography are sodium carbonate, potassium carbonate and the caustic alkalies sodium and potassium hydroxide. The quantity and the character of the alkalies exert a profound influence on the properties of developers. There is a notable difference between the action of the alkali carbonates, that is, sodium and potassium carbonates, and the caustic alkalies, the latter giving developers of much greater energy than the carbonates.

### *Sodium Carbonate*

This is the most widely used of all the alkalies, and appears on the market in three forms.

Crystal sodium carbonate, contains ten molecules of water and so is called deca-hydrated and has about 37 per cent by weight of anhydrous sodium carbonate.

Next there is anhydrous or desiccated sodium carbonate which theoretically is free from water and contains nominally about 98 per cent pure sodium carbonate.

The third form contains one molecule of water and is termed mono-hydrated sodium carbonate, and contains 85 per cent by weight of anhydrous carbonate. The equivalent weight relation which these three varieties bear to one another is shown in the following table.

#### IV.—EQUIVALENT QUANTITIES OF CRYSTALLINE AND ANHYDROUS SALTS

100 parts by weight of crystal sodium carbonate	=	37½ parts by weight of anhydrous
" " " " " " " "	=	85½ parts by weight of monohydrate
100 parts by weight of anhydrous sodium carbonate	=	270 parts by weight of crystal salt
" " " " " " " "	=	120 parts by weight of monohydrate

These equivalents are not exact, but are quite near enough for all practical purposes.

### *Potassium Carbonate*

Potassium carbonate, or carbonate of potash, occurs only in one form, the anhydrous salt. It is, however, a very hygroscopic material which absorbs water rapidly from a moist atmosphere. Hence it should never be kept in paper packets but always in bottles with either a close-fitting glass stopper or better still a well-waxed and sound cork.

In general there is nothing to be gained by substituting potassium carbonate for sodium carbonate in developer solutions. Where it has an advantage is in the preparation of

concentrated developers, as its solubility is much greater than that of sodium carbonate. It can be used in practically the same proportions, or more exactly 13 parts by weight of the potassium carbonate are equal to 10 parts by weight of sodium carbonate.

### *Caustic Alkalies*

These are much more energetic in their action than the alkali carbonates, and are only used in those cases where a powerful and quick-acting developer is required. As might be expected, developers compounded with caustic alkali have poor keeping properties and are soon exhausted. The reason for this difference in properties between developers compounded with carbonates and those made with caustic alkalies is of sufficient interest to call for a little special explanation.

When sodium carbonate is dissolved in water, part of it is split up, or as the chemist calls it, hydrolysed. As a result, caustic soda and bicarbonate of soda are formed although only in small quantities at any one moment. When development is taking place the caustic soda or sodium hydroxide is used up and as that happens more carbonate hydrolyses. Hence the carbonate acts as a sort of reservoir of caustic alkali. If we had caustic soda in place of the carbonate to give the same alkalinity, it would soon be used up and the activity of the developer would cease. Obviously the use of sodium carbonate allows us to use a small concentration of alkali and get the utmost work out of it. The above explanation also shows why it is rarely possible to substitute caustic alkalies for carbonates in normal developers.

As their name implies, caustic alkalies possess corrosive properties, a fact which must be remembered when handling them. They can burn the skin, are very dangerous to the eyes and act vigorously on other materials of both organic and inorganic origin. They are also intensely hygroscopic and so must be preserved from contact with moist air if they are to be kept in solid form. They are usually sold in sticks which are kept in bottles with well-fitting waxed corks, or in pellet form in tins with close-fitting lids.

There is no difference between the potassium and sodium hydroxides so far as photographic uses are concerned, other

than that 10 parts by weight of the sodium salt are the equivalent of 14 parts by weight of the potassium.

Among other energetic alkalies mention may be made of sodium metasilicate (Metso). This substance, as the table on page 90 shows, is almost as alkaline as the hydroxides and equal to the carbonate. It has the advantage that it does not attack gelatine and also that it tends to reduce any excessive swelling. As a result it helps toward the quick drying of films developed in formulae containing it.

### *Substitution of Alkalies*

We have already given the proportions in which one alkali can be substituted for another, but it will be realised that such substitution is only possible between members of the same group. For example, one can substitute one carbonate for another, or one caustic alkali for another, but it is not possible to substitute the alkali of one group by that of another group.

Of late years another form of substitution has come into use, and in some formulae one finds formalin or paraformaldehyde substituted for caustic alkali. Formalin is a solution of formaldehyde gas in water (40% w/v.) and paraformaldehyde is a white powder which produces formalin when dissolved in water. One of the most useful properties of formalin is its hardening effect on gelatine, and it is widely used for hardening the emulsion of photographic materials. It can exercise this property when added to a developer, but it also has another action. It reacts with sodium sulphite and one of the products of that reaction is sodium hydroxide.

Formaldehyde + sodium sulphite + water = Formaldehyde-bisulphite + sodium hydroxide. Hence the result of adding formalin to a developer containing sulphite but no alkali is equivalent to adding caustic soda to the developer. It is mainly used to prepare highly active and contrasty hydroquinone developers.

The formaldehyde-bisulphite compounds keep the sulphite concentration at a low and constant level. The keeping qualities of the developer are not seriously affected, but the hydroquinone is more easily oxidised to quinone and semiquinone. The latter acts as an accelerator causing rapid development of silver halide grains and also a reduction of

grains adjacent to those already developed. This process of "infectious" development gives gradation curves with very high gamma and short toe as required for lith materials.

### *Mild Alkalies*

For some years now another group of alkalies has found application in photographic practice to which the name "mild alkalies" might be given. Of these the most widely used is borax, or sodium biborate, which finds its widest use in the compounding of fine-grain developers.

Another compound which falls in this group is Kodalk introduced by Kodak, which is more alkaline than borax and somewhat more easily soluble, but less alkaline than carbonate. When used as a substitute for carbonate, two parts by weight of Kodalk are the equivalent of one part by weight of carbonate in normal developers. As Kodalk contains no free carbonate there is no danger of bubbles of carbonic acid gas being formed when an acid stop-bath is used, a very real advantage in certain circumstances. (For formulae containing Kodalk, see page 206.) Kodalk is identical with sodium metaborate.

In the chapter on fine-grain developers certain other mild alkalies will be discussed as well as organic substances such as triethanolamine, acetone, etc. The properties of tribasic sodium phosphate, the action of which lies between that of carbonate and caustic alkalies, will also be dealt with.

### ALKALIES AND pH VALUES

So far in this book we have spoken of alkalies as caustic, energetic or mild, a description which from a scientific standpoint leaves much to be desired. The alkalinity or acidity of any solution can be exactly measured and equally exactly described in terms of its pH value (see page 115). A full understanding of exactly what is meant by pH value\* is not necessary for the photographer; it is sufficient to know that pure water, which is neither acid nor alkaline but neutral, has a pH value of 7, that any pH below 7 indicates acid or above 7 indicates alkaline and that the higher the pH value the more alkaline the solution.

\*V. Gold, *pH Measurements, their Theory and Practice*, Methuen, London, 1956.

## V.—pH-VALUES

pH-value	Solution is.
0—2	strongly acid
3—4	acid
5—6	weakly acid
7	neutral (pure water)
8—9	weakly alkaline
10—11	alkaline
12—14	strongly alkaline

In Table VI (page 90), pH values are given for a series of alkalies and preservatives, mixtures of these developer constituents, and processing solutions.

Where the percentage strength of solutions is not given the value relates to saturated solutions.

Although in the table the differences between the pH values of the various solutions appears small remember that the pH figures are logarithm values and so a solution of pH 10 is ten times more alkaline than a solution having a pH value of 9. This latter in turn is ten times as alkaline as a solution with a pH value of 8 and so on, thus a small change in pH indicates a notable variation in alkalinity. As the table shows, the pH values of developers cover a very wide range from strongly alkaline through weaker and very weak alkaline to neutral.

The table also allows us to draw a conclusion of particular value in connection with fine-grain developers. As we shall see later (page 202) solutions of low alkalinity are important for fine-grain developers. In the preparation of such solutions two possibilities offer themselves. Either we can use a strong alkali in weak concentration or a mild alkali in higher concentration, for example we can take a 0.1% solution of sodium carbonate or even weaker, or a 0.2% or stronger solution of borax. Which will give us the best result?

The answer is that we shall obtain a more constant working and a better keeping developer by using a mild alkali at relatively high concentration than if we use a weak solution of a strong alkali. Similar considerations enter into the use of the so-called "Buffer-mixtures" in developers. Perhaps the best known example is the Buffered Borax Developer No. 84 (page 206). This formula contains a relatively large quantity of borax as alkali and in addition a quantity of acid, namely boric acid. This has the effect of stabilising

## VI.—pH VALUES OF CHEMICALS AND SOLUTIONS

### *Alkalies*

Sodium hydroxide 4%, potassium hydroxide 5.6%	14.0
Sodium hydroxide 0.4%, potassium hydroxide 0.5%	13.0
Sodium hydroxide 0.04%, potassium hydroxide 0.05%	12.0
Sodium carbonate 5—10%	11.5—11.6
Potassium carbonate 5—10%	11.6
Trisodium phosphate 3—4%	12.0
Trisodium phosphate 1%	11.3
Sodium metaborate 1—5%	10.5—10.8
Sodium metasilicate 1%	12.6
Sodium metasilicate 0.1%	11.5
Ammonia 3—4%	11.6
Ammonia 0.3%	11.1
Ammonia 0.03%	10.6
Borax 0.1%	9.5
Kodalk 0.2%	9.9
Sodium sulphite 5—10%	8.0—9.9
Triethanolamine 10%	10.6
Disodium hydrogen sulphate 1%	8.0
Sodium sulphite 10% + borax 0.2%	9.5
Sodium sulphite 10% + borax 0.2% + Boric acid 1.4%	8.1

### *Acids*

Hydrochloric acid 3—4%	1.1
Sulphuric acid 1%	1.2
Citric acid 2%	2.2
Acetic acid 6%	2.4
Acetic acid 0.6%	2.9
Acetic acid 0.06%	3.4
Potassium alum 5%	3.2
Boric acid 0.5%	5.2
Sodium dihydrogen phosphate 1%	4.2
Sodium metabisulphite 1%, potassium metabisulphite 1%	4.3—4.9

### *Buffer Mixtures*

Acetic acetate, sodium acetate	4.6
Potassium dihydrogen phosphate, disodium phosphate	6.8
Boric acid, borax	8.5
Boric acid, sodium hydroxide	9.2
Disodium phosphate, sodium hydroxide	11.5

### *Processing Solutions*

Hydroquinone and p-aminophenol developer with hydroxide	12.0—12.5
M.Q.-sodium carbonate	10.0—10.5
M.Q.-borax	8.6
M.Q.-buffered borax	7.9
Metol—sodium sulphite with bisulphite	7.2

### *Hardening fixing baths*

Acid fixer	4.8
Stop bath with potassium metabisulphite	4.6
Stop bath with acetic acid	2.9



the pH value and acting as a buffer against any violent change, hence its name. Such developers are characterised by their constant and even working properties as well as good working life.

#### RESTRAINERS

The great majority of developers fulfil, more or less completely, the important function of acting only on the exposed silver bromide in sensitive materials and leave unattacked that portion of the emulsion which has not received any exposure. Their action is selective and does not lead to a general fogging of the whole of the sensitive surface.

In order to ensure that they shall produce an image completely free from fog, a restrainer is made use of and the substance most widely used for this purpose is potassium bromide.

#### *Potassium Bromide*

acts not only as a fog preventer but also as a restrainer, that is, it slows down the rate of development. This action varies with different developers. In many cases the restraining action is very strong, in others the effect is only small. It is important to remember this difference and take it into account when compounding developers for special or even general purposes.

In the following table there are set out examples of the relative lengthening of development time caused by the addition of an equal quantity of potassium bromide.

It will be seen that a metol-carbonate developer is relatively insensitive to the action of potassium bromide whereas a hydroquinone-caustic developer is strongly affected and the development time notably prolonged. This emphasises the important fact that the effect of potassium bromide as a restrainer depends almost wholly on the composition of the developer. It should also be remembered that the addition of potassium bromide usually results in a reduction of the contrast in the developed image. Excessive bromide may thus produce as undesirable an effect as slight fogging.

## VII.—LENGTHENING OF DEVELOPMENT TIME BY THE ADDITION OF POTASSIUM BROMIDE

Developer	Percentage lengthening of development time
Glycin-potassium carbonate	300%
Glycin-caustic soda	200%
Hydroquinone-caustic soda	400%
p-Aminophenol-potassium carbonate	17%
Amidol	150%
Hydroquinone-potassium carbonate	140%
p-Aminophenol-caustic potash	100%
Pyrogallol-potassium carbonate	80%
Metol-potassium carbonate	25%

### *Various Restrainers*

Some formulae contain potassium iodide which also acts as a restrainer and an anti-fogging agent, but the quantity should always be very small, very much less relatively than is permissible with potassium bromide. Potassium iodide in appreciable quantities is a disadvantage because it produces silver iodide in the sensitive material which is not very soluble in fixing baths and so lengthens unduly the fixing time. On the whole the use of potassium iodide as a restrainer is not recommended.

Certain organic compounds, notably nitrobenzimidazole and benzotriazole, have the interesting properties of acting as anti-fogging agents without affecting in any way other properties of the developer. They are used in very small quantities, one part in ten thousand of the developer being a perfectly satisfactory proportion to use.

The use of compounds of this type is sound practice in every-day work, as they afford real protection against any tendency to fogging by the developer itself, or by variations in its preparation, too high temperature or even prolonged development. They also have an excellent effect when somewhat stale or badly stored sensitive material has to be used.

### OTHER ADDITIONS TO DEVELOPERS

When hard water is used for the compounding of developers a milkiness or turbidity is often produced; this is caused by the action of alkali carbonate and sulphite on the lime salts

present in the water. If the amount of lime salt is excessive a troublesome precipitate of calcium carbonate and sulphite may be deposited on the sensitive film unless the developer has been filtered or the precipitate destroyed in some other manner. The formation of this precipitate of carbonate of lime can be prevented by the addition of certain sequestering agents.

Calgon is a proprietary compound put on the market for this purpose; it is essentially sodium hexametaphosphate and is added to the developer solution. In general, one part per thousand is sufficient, except for very hard water. Where the amount of lime present is high the proportion of Calgon can be slightly increased. For the same purpose EDTA—ethylenediaminetetraacetic acid—can be used.

#### WETTING AGENTS

Wetting agents are used in many branches of industry with most useful results and in recent times have found successful application for photographic purposes, particularly as additions to developers.

In order to understand the action of a “wetting” agent we must know what the operation of wetting really is. It may be defined as the forming of a continuous adsorbed film of liquid upon the surface of any desired solid or on that of another liquid. The capacity of a liquid for wetting depends to a large extent upon its surface properties.

The surface or interface of a liquid where, for example, it is in contact with air, behaves differently from the liquid layers lying beneath it. If a needle be stroked by the fingers sufficient grease will remain or be transferred to the needle to repel water and allow it to float so long as it is laid down carefully lengthwise on water. If, however, one end be pressed so that it penetrates the water the needle instantly sinks. Thus the surface of the water behaves as though it were a thin membrane and resisted rupture. There is, in fact, a force, which is called surface tension, acting along the surface of the water which tends to prevent the surface being broken. This surface tension is also the force which tends to prevent liquids from spreading evenly over a surface and so wetting it completely and evenly. Wetting agents are substances which have the power of lessening this surface

tension and so facilitating the spreading or wetting of a liquid or another surface.

A simple experiment will demonstrate this. If we take a vessel full of water and plunge a piece of old film into it, quickly withdrawing the film we shall see that the whole of the surface of the film is by no means wetted, that on the contrary the moistening has only been in patches here and there. If now we repeat the experiment with the difference that we add a wetting agent to the water, usually one part per thousand is ample, we at once observe a very notable difference for the whole surface of the film is now covered by a complete even film of water.

Of what benefit will this wetting effect be in practice?

The first and obvious advantage is in the assurance of a quick and even wetting of film or plate in the developer and the safeguarding in this way against air bubbles or bells and other inequalities of wetting. This is of quite special importance when using daylight developing tanks (page 145) in which the spiral leads for the film leave but little space for contact between film and developer. Quick and even wetting of the film is equally of importance for high speed development as described on page 233. Wetting agents, suitable for photographic purposes, are commercially available. Most of them belong to the group of sulphonate, sulphated or carboxylated fatty alcohols.

#### ORGANIC ACCELERATORS

The charge barrier of the silver halide grain can be neutralised or even completely changed by a different class of agents which have no developing action whatsoever but are strongly electroactive and possess a positive charge, accelerating the action of the developer. This effect can be produced by certain cationic surface active agents of the quaternary type in a concentration of about 0.05-0.1 %. Suitable compounds are for instance:

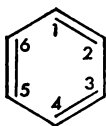
Cetyl-trimethyl-ammonium bromide (Cetavlon)  
Cetyl-pyridinium bromide  
Dimethyl-benzyl-lauryl-ammonium chloride  
Lauryl-pyridinium chloride  
Lauryl-pyridinium-p-toluene sulphonate  
Beta-phenylethyl-alpha-picolinium bromide.

These agents are only effective in developers which have normally a noticeable induction period, i.e. a negative charge, for instance hydroquinone or to a lesser degree metol. They are of no use for developing agents which have no charge and practically no induction period, such as p-phenylenediamine and its derivatives (see page 104).

## DEVELOPING AGENTS

We have already learned that developing agents or substances are reducers (see page 22), but that not every reducing agent can act as a photographic developer. For a reducing agent to act as a developer it must possess the property of reducing only the exposed silver bromide and of leaving the unexposed material unaltered.

Fortunately there are many compounds which possess this quality, although they differ notably in both chemical and photographic properties and their action is to a very large degree dependent on the composition of the developer in which they play the part of reducing agent. From the chemical point of view, reducing agents have to fulfil a number of conditions to be suitable as developing agents. Aromatic organic compounds must have either two hydroxy (OH) groups or two amino (NH<sub>2</sub>) groups or one hydroxy and one amino group. Aromatic compounds can be considered as those organic compounds that possess a benzene nucleus:



Only ortho and para compounds have developing action but not meta compounds. Ortho (o) compounds are those compounds that have two substituents in the 1 and 2 (or 1 and 6) positions of the benzene nucleus, para (p) compounds have two substituents in the 1 and 4 positions and meta (m) compounds are 1:3 (or 1:5) disubstituted benzene compounds. The hydrogen atoms of the amino group can be replaced by alkyl groups but not those in the hydroxy group which would destroy the developing power. If, however, the hydrogen atoms of the benzene nucleus are replaced by alkyl or halogen or

further hydroxy or  $\text{NH}_2$  groups the developing power is not decreased but may be increased. The same rules are true for naphthalene derivatives but there are no developing agents of practical importance in this group.

In judging the properties of developing agents the following points are all of importance and due consideration must be given to them.

- (1) Solubility.
- (2) Fogging effect and/or discoloration of film or fingers.
- (3) Reaction to changes of temperature.
- (4) Reaction to bromide addition.
- (5) Behaviour with carbonate and caustic alkalies.
- (6) Keeping properties and rate of exhaustion.
- (7) Influence on graininess.
- (8) Toxicity.
- (9) Cost.

### *J Metol*

#### N-Methyl-p-aminophenol sulphate

Metol is easily soluble in water and permits the preparation of concentrated stock solutions. If these are beyond a certain concentration a precipitation of the metol base by the alkali sulphite may occur. This can be remedied either by ensuring that the whole of the metol is dissolved before any further addition is made or by the addition of alcohol in the proportion of one-tenth by volume to the solution.

Acetone can also be used in even smaller proportion, namely 55 parts per 1,000.

Metol responds well to the addition of bromide, giving a very clean working developer without any staining of either film or fingers. The energy of the developer is only slightly affected by low temperature, and is also but slightly reduced by the addition of bromide.

Metol alone with either sodium or potassium carbonates gives a rapid working developer when the alkalies are in high concentration, but the speed of development can easily be controlled by dilution.

The use of caustic alkali with metol is not recommended as there is a tendency to excessive fog.

When used with sulphite alone without alkali, metol

provides a slow-working, fine-grain developer, but it is preferable to use a mild alkali such as borax, which accelerates the rate of development without increasing the grain-size of the image appreciably.

Developers containing metol as the sole developing agent are not very widely used, but in combination with hydroquinone it provides the most widely used developer.

All metol developers keep well and are only slowly exhausted.

Metol had the reputation of causing skin poisoning (dermatitis); this was traced to certain impurities and not to the metol itself. Today good quality metol is free from such impurities, but some people are even sensitive to the purest type. p-Aminophenol developers are free from this trouble, and can thus be used instead of metol developers which they resemble. Still better, use Phenidone developers (page 198) or amidol developers (page 99).

### ✓ *Hydroquinone* p-Dihydroxybenzene

Hydroquinone is fairly soluble in cold, easily soluble in warm water. In general it is a clean-working and non-staining developer.

In some respects its properties are in marked contrast to those of metol: it is notably affected by low temperature and below 50°F. (10°C.) its action slows down very considerably. It is also extremely susceptible to the action of bromide. When compounded with alkali carbonates it gives somewhat slow-working but contrasty developers, while with caustic alkalies its action is very rapid and gives the highest possible contrast. For this reason it is the most widely used developer in technical practice, especially in process work where the highest attainable contrast is essential. In the presence of caustic alkali, i.e. at high pH, it is not especially temperature sensitive and can be used for low-temperature developing.

Hydroquinone developers keep reasonably well and are only slowly exhausted.

In normal photographic practice hydroquinone alone is not largely used, but in combination with metol or Phenidone it provides a universal developer of outstanding value. By varying the relative quantities of metol and hydroquinone

and adjusting the quantities of sulphite and carbonate, almost any desired contrast or rate of development can be obtained (see page 173). The combination can also be used as a fine-grain developer by suitably modifying the formula.

✓ *Chlorquinol*  
Chlorhydroquinone

Less soluble in cold water than hydroquinone, but easily soluble in hot water, rather more energetic in action than hydroquinone and almost equally sensitive to the action of bromide.

Its main use is as a warm-tone developer for papers when heavily restrained with bromide. As a negative developer it has no advantage over metol-hydroquinone.

✓ *Pyrocatechin*  
Catechol, o-Dihydroxybenzene

Easily soluble in warm water, chemically closely akin to hydroquinone but with some quite special properties, notably the fact that it oxidises very readily and its oxidation products tan gelatine. When used without sulphite or with very low sulphite content it gives a heavily stained image and tans the gelatine in proportion to the density of the image. This property has led to its use for a number of special purposes, such as high-definition and tanning developers, for a description of which see pages 214 and 222.

Pyrocatechin with caustic alkali provides a very rapid developer.

✓ *Pyrogallol*  
Pyrogallic acid, Pyro. 1, 2, 3-Trihydroxybenzene

Readily soluble in water, very easily oxidised, and the oxidation products tan gelatine and also colour the film and stain the fingers. Pyrogallol was at one time a universally used developer, but today equal results can be obtained by modern developers without the disadvantages of pyrogallol, which has poor keeping qualities.

In combination with metol it has some vogue among press



photographers on account of its rapid action and the belief that the yellow stain on the film adds printing quality. It is also used for tanning developers.

Pyrogallol in combination with Phenidone has been shown to exhibit superadditivity (see page 101) and to be quite stable when left in an open tray overnight.\*



#### *Glycin*

##### *p-Hydroxyphenyl glycine*

Almost insoluble in water but dissolves readily in alkaline solutions. Oxidises very slowly, very clean working. Used mainly in developers for papers until fine-grain developers assumed importance; now sometimes used in combination with other developers for this purpose.

Glycin is very sensitive to bromide and also to low temperature; with alkali carbonates it makes slow-working developers which have good keeping properties and give low contrast.



#### *p-Aminophenol hydrochloride*

Very soluble in cold water, its principal use is in the preparation of very concentrated developers with caustic alkalis which will stand dilution from 20 to 100 times. These concentrated solutions keep well and should only be diluted immediately before use.

They work rapidly, are free from fogging properties and do not stain. They are not sensitive to variations of temperature nor do higher temperatures affect their clean working. They can, however, cause excessive swelling at high temperature because of high pH and low concentration. The diluted solutions are suitable as high-definition developers.

Alkali carbonate should not be used with this substance as they precipitate out the base and prevent the preparation of any but very dilute solutions.

#### *Amidol*

##### ✓ Diaminophenol. 2 : 4 Diaminophenol hydrochloride

Very soluble in water or in sulphite solution. Amidol has the interesting property of acting as a developer in sulphite

\*M. Levy, Photogr. J., 105, 303 (1965).

solution without the necessity of adding any alkali. The solution is easily prepared but does not keep, although its keeping properties may be somewhat improved by the addition of a weak acid such as lactic acid. Solutions of amidol with bisulphite have the noteworthy property of beginning their development in the depth of the film and not, as is usually the case, at the surface. So far no practical use appears to have been made of this depth-development effect.

As amidol develops in the absence of alkali there is not the excessive swelling of the film that takes place with other developers and amidol is therefore favoured as a tropical or high temperature developer, although it is possible to prepare other developers having like properties without the disadvantage of the poor keeping properties of amidol.

J     *p*-Phenylenediamine  
1:4 Diaminobenzene

Only slightly soluble in water when in the form of the base, but much more soluble as the hydrochloride salt. Its particularly valuable property is that it supplies a very fine-grain developer. For various formulae with *p*-phenylenediamine alone, and in combination with other developer substances, see page 210.

Unfortunately *p*-phenylenediamine suffers from a number of drawbacks: it is poisonous and has also a very strong tendency to staining and wherever a particle of powder rests it causes a brown spot very difficult to remove. It will also stain both film and fingers unless very carefully handled.

These many disadvantages have naturally led to attempts at discovering developers which would give fine-grain developers without the troublesome properties. One such material is *o*-phenylenediamine which must, however, be quite free from any trace of the para compound (see page 209).

*p*-Phenylenediamine forms addition products with various other developing agents, in particular with hydroquinone and pyrocatechin. To this group belongs Meritol, a fine-grain developer which is less poisonous and less staining than *p*-phenylenediamine. Derivatives of *p*-phenylenediamine have found wide application for colour development (see page 366).

J

### *Phenidone*

#### *1-phenyl-3-pyrazolidone*

Phenidone is a colourless crystalline compound which is moderately soluble in hot and slightly in cold water. It is, however, readily soluble in both aqueous acids and alkalies, including solutions of alkali bisulphites and carbonates, so that it can easily be incorporated into developer solutions. When used alone in sodium carbonate-sulphite solutions, it gives very fast but extremely soft working developers. The developing properties of Phenidone (Trade Mark registered by Ilford) were discovered by J. D. Kendall, who worked out a process suitable for the large-scale manufacture of this compound. In mixture with hydroquinone, Phenidone is highly active and retains its activity well. Phenidone has a low oral toxicity and is unlikely to cause dermatitis. Sufferers from metol poisoning have been able to use Phenidone developers without any ill effects.

### SUPERADDITIVITY

The phenomenon of superadditivity is of the greatest importance for the formulation of modern developers. As a matter of fact, by far the majority of all developers in use today are based on this effect.

Developing agents are said to be superadditive if the sum of their combined action is greater than the sum of their actions used separately. The best known example of such a superadditive combination is metol-hydroquinone. Metol is—as we already know (page 96)—a developing agent of fast action, while hydroquinone develops slowly. If we combine them in one formula, however, we obtain a developer which can be still faster than metol alone and which can produce contrast equal to or even higher than that of hydroquinone alone.

This phenomenon is still more pronounced in the combination Phenidone-hydroquinone. Phenidone on its own is quite useless as a developer; it acts fast but the contrast of the negative is very low. Added in a comparatively small quantity to a hydroquinone developer, however Phenidone retains its high activity and combines with it the contrast hydroquinone is able to produce.

**VIII.—CHARACTERISTICS OF**  
*A In alkaline carbonate solution.      B In caustic*

<i>Developer</i>		<i>(1) Fog formation and staining</i>	<i>(2) sensitivity to temperature</i>	<i>(3) sensitivity to bromide</i>
METOL	A	none	slight	slight
	B	appreciable	slight	slight
	C	none	moderate	moderate
HYDROQUINONE	A	none	strong	strong
	B	none	moderate	moderate
	C	not suitable	—	—
PYROCATECHIN	A	none	strong	strong
	B	none	slight	slight
	C	not suitable	—	—
PYROGALLOL	A	stains	moderate	moderate
	B	not suitable	—	—
	C	not suitable	—	—
AMIDOL	A	none	moderate	moderate
	B	not suitable	—	—
	C	not suitable	—	—
PHENIDONE	A	none	slight	slight
GLYCIN	A	none	very strong	very strong
	B	none	strong	strong
	C	not suitable	—	—
P-AMINOPHENOL	A	not suitable	—	—
	B	none	slight	slight
	C	not suitable	—	—
CHLORQUINOL	A	none	moderate	moderate
	B	none	slight	slight
	C	not suitable	—	—
P-PHENYLENE-DIAMINE	C	strong staining properties	moderate	moderate
O-PHENYLENE-DIAMINE	C	none	moderate	moderate

# DEVELOPING AGENTS

alkali solution.

C As a fine-grain developer.

(4) Speed of development	(5) Gradation	(6) Keeping properties (a) separately (b) mixed	(7) Properties See pages	(8) Examples of Formulae See Nos.
normal-rapid rapid slow	soft soft soft	a and b good a good, b bad a and b good	93	1—29
slow rapid —	contrasty contrasty —	a and b good a good, b bad —	94	1—29 30—37
normal rapid —	normal contrasty —	a and b good a good, b bad —	95	43—44
normal — —	soft — —	a good, b bad — —	95	45
normal — —	normal — —	solutions do not keep — —	96	54
normal	soft	a and b good	97	55—62
slow rapid —	normal-soft normal —	a and b good a good, b bad —	95	46—49
— normal-rapid —	— normal-soft —	— a good, b bad —	96	50—53
normal rapid —	normal contrasty —	a and b good a good b bad —	94	40—42
slow	soft	varies with formula	97	95
slow	soft	good	97	98

The maximum developing speed is reached when the developer contains 7% Phenidone based on its hydroquinone contents. Such a developer is 50% faster than a metol-hydroquinone developer under comparable conditions, i.e. containing the optimum quantity of 28% metol with regard to hydroquinone. As a matter of fact, Phenidone is about 18 times more efficient as an activator than metol.

At a practically useful Phenidone to hydroquinone ratio, Phenidone has the tendency to produce fog. This fog can, however, easily be controlled by the addition of organic restrainers (page 92), such as benzotriazole, used in a quantity of 0.1-0.2 gram per litre of developer.

#### INDUCTION PERIOD

To understand the phenomenon of superadditivity and also the influence of certain agents on the course of development (see page 94), we have to consider the surface condition of the silver halide grain in the emulsion. Development can obviously only take place if the developing agent can reach the surface of the silver halide grain.

However, the developer is opposed by an electrostatic effect, and can not easily penetrate to the surface of the grain. This electrostatic effect is caused by a negative charge barrier which surrounds the grain and tries to prevent the approach of negatively charged agents such as the developing substance. Thus an induction period is produced varying with the magnitude of the charge of the developing agent.

According to the length of the induction period developing agents can be divided into the following groups:

- (A) Developing agents with no charge, such as p-phenylendiamine and derivatives.
- (B) Developing agents with one negative charge, such as metol and Phenidone.
- (C) Developing agents with two negative charges, such as hydroquinone.

The developing agents in group (A) have practically no induction period. Beginning immediately, the developing process is at first rapid but soon slows down. Contrast and maximum density of the negatives are very low. Developing agents of group (B) start to react with some delay; develop-

ment increases proportionally but the negatives have a tendency to be soft. Developers of group (C) have a noticeable induction period and start very slowly. Once a certain density is reached, the density increases with development time. The negatives have normal to high contrast.

The induction period can be explained in terms of a change in the magnitude of the charge barrier surrounding the silver halide grain. As the charge barrier is reduced, a larger quantity of the developer can reach the surface and the rate of reaction is increased. Developing agents with no charge are not hindered by the barrier and the developer does not show an induction period.

The phenomenon of superadditivity can be explained, at least partially, by the effect which developing agents of group (B) have on the potential barrier of the grain. By breaking the barrier down, they reduce the induction period and once this has been done, the developing agents of group (C) can take over and carry on the development of the grain.

However, this process alone does not seem to explain the powerful effect of Phenidone and similar substances which is probably due to a triple action. First, the barrier layer effect, as explained above. Secondly, a chemical reaction, during which hydroquinone regenerates the Phenidone from its reaction products. Thirdly, the formation of products which can accelerate development. This intermediate product has a positive charge and will therefore decrease very efficiently the charge of the barrier, thus facilitating the approach of the negatively charged developing agent.

More recently it has been suggested that charge barrier effects are less important than was previously supposed and that the major contributory factor is the regeneration of the primary developing agent (e.g. Phenidone or metol) at the grain surface by the secondary developing agent (e.g. hydroquinone).

# *Preparing Solutions*

## CHEMICALS

The first point is to see that the chemicals used are of first-class quality and are obtained from a dependable dealer. It is more economical to buy in large than in small quantities, but here the photographer must be guided by the amounts of each chemical he is likely to use, and also by the keeping properties of the chemicals. It must also be emphasised that no chemical should be kept in paper packets or bags, in which it will be exposed to the more or less damp atmosphere of the dark-room.

## ORDER OF DISSOLVING

It is usually of the greatest importance to dissolve constituents in the order given in the formula.

Generally it is convenient to dissolve the sulphite first because most developing agents are easily oxidised in water in the absence of this preservative.

An exception to this is the case of metol which (see page 96) is only soluble with difficulty in sulphite solutions. Hence when making up developers containing metol, it should be dissolved before the sulphite. This has no serious effect on the keeping properties of the developer as metol itself is not very easily oxidised.

Many practical workers prefer to dissolve a pinch of sulphite, or a crystal or two of metabisulphite, in the water before dissolving the metol. In such cases the small extra amount of sulphite is ignored; it is insufficient to upset the balance between sulphite and alkali in the finished developer.

A basic rule in preparing developers is to make quite



certain that each constituent in turn is completely dissolved before the next is added.

Where developers are bought in packet form this rule cannot be obeyed in full because the packets do not contain separate constituents, but usually consist of a small package containing the developing agents and a much larger one containing the other constituents. Even so, the rule can be followed by dissolving the contents of the small packet first and ensuring that the contents are completely dissolved before the contents of the larger packet are added to the solution.

#### TEMPERATURE

With some few exceptions that do not interest us here, all chemicals have the property of dissolving more rapidly and more easily in warm water than in cold. Note that we say warm, for it would be a mistake to go too far and to use boiling water. In many cases this would cause decomposition of the materials with the possible precipitation of insoluble residues which would interfere with the properties of the developer and with the development process. It must also be remembered that too high a temperature accelerates the tendency to oxidation and so reduces the keeping properties of the solution.

When using warm water in the preparation of developer, etc., it is not necessary to employ the whole volume called for by the formula; it is preferable to use about two-thirds and then to make up to the required volume with cold water when solution is complete. Many modern formulae are set out in this manner.

The temperature of a solution should not exceed 120°F. (50°C.) unless the instructions with the formula definitely prescribe a higher temperature.

When solution is complete the developer should be cooled to normal temperature. By normal temperature is meant that temperature at which processes such as development and the like should be carried out, and that is taken as 68°F. (20°C.) in this book. A degree or two above or below this temperature is not of great importance, but every endeavour should be made to keep the temperature of the solutions as close as possible to 68°F. when in use.

It should also be noted that where solutions have been

# IX.—FAHRENHEIT AND CENTIGRADE

F.	C.	F.	C.	F.	C.
+212	+100	+169	+76.11	+126	+52.22
211	99.44	168	75.55	125	51.67
210	98.89	167	75	124	51.11
209	98.33	166	74.44	123	50.55
208	97.78	165	73.89	122	50
207	97.22	164	73.33	121	49.44
206	96.67	163	72.78	120	48.89
205	96.11	162	72.22	119	48.33
204	95.55	161	71.67	118	47.78
203	95	160	71.11	117	47.22
202	94.44	159	70.55	116	46.67
201	93.89	158	70	115	46.11
200	93.33	157	69.44	114	45.55
199	92.78	156	68.89	113	45
198	92.22	155	68.33	112	44.44
197	91.67	154	67.78	111	43.89
196	91.11	153	67.22	110	43.33
195	90.55	152	66.67	109	42.78
194	90	151	66.11	108	42.22
193	89.44	150	65.55	107	41.67
192	88.89	149	65	106	41.11
191	88.33	148	64.44	105	40.55
190	87.78	147	63.89	104	40
189	87.22	146	63.33	103	39.44
188	86.67	145	62.78	102	38.89
187	86.11	144	62.22	101	38.33
186	85.55	143	61.67	100	37.78
185	85	142	61.11	99	37.22
184	84.44	141	60.55	98	36.67
183	83.89	140	60	97	36.11
182	83.33	139	59.44	96	35.55
181	82.78	138	58.89	95	35
180	82.22	137	58.33	94	34.44
179	81.67	136	57.78	93	33.89
178	81.11	135	57.22	92	33.33
177	80.55	134	56.67	91	32.78
176	80	133	56.11	90	32.22
175	79.44	132	55.55	89	31.67
174	78.89	131	55	88	31.11
173	78.33	130	54.44	87	30.55
172	77.78	129	53.89	86	30
171	77.22	128	53.33	85	29.44
170	76.67	127	52.78	84	28.89

# DEGREES OF TEMPERATURE

F.	C.	F.	C.	F.	C.
+83	+28.33	+41	+5	— 1	—18.33
82	27.78	40	4.44	2	18.89
81	27.22	39	3.89	3	19.44
80	26.67	38	3.33	4	20
79	26.11	37	2.78	5	20.55
78	25.55	36	2.22	6	21.11
77	25	35	1.67	7	21.67
76	24.44	34	1.11	8	22.22
75	23.89	33	+0.55	9	22.78
74	23.33	32	0	10	23.33
73	22.78	31	—0.55	11	23.89
72	22.22	30	1.11	12	24.44
71	21.67	29	1.67	13	25
70	21.11	28	2.22	14	25.55
69	20.55	27	2.78	15	26.11
68	20	26	3.33	16	26.67
67	19.44	25	3.89	17	27.22
66	18.89	24	4.44	18	27.78
65	18.33	23	5	19	28.33
64	17.78	22	5.55	20	28.89
63	17.22	21	6.11	21	29.44
62	16.67	20	6.67	22	30
61	16.11	19	7.22	23	30.55
60	15.55	18	7.78	24	31.11
59	15	17	8.33	25	31.67
58	14.44	16	8.89	26	32.22
57	13.89	15	9.44	27	32.78
56	13.33	14	10	28	33.33
55	12.78	13	10.55	29	33.89
54	12.22	12	11.11	30	34.44
53	11.67	11	11.67	31	35
52	11.11	10	12.22	32	35.55
51	10.55	9	12.78	33	36.11
50	10	8	13.33	34	36.67
49	9.44	7	13.89	35	37.22
48	8.89	6	14.44	36	37.78
47	8.33	5	15	37	38.33
46	7.78	4	15.55	38	38.89
45	7.22	3	16.11	39	39.44
44	6.67	2	16.67	40	40
43	6.11	1	17.22		
42	5.55	0	17.78		

over-cooled, or when they have been kept in a cold place, crystallisation of some of the constituents may occur; this should be guarded against as much as possible.

#### MANIPULATION

Solutions should not be prepared in the vessels in which they are to be used, e.g., tanks, dishes, etc., but in separate vessels. Glass or porcelain jars or wide-mouthed bottles are convenient, but metal receptacles other than stainless steel should not be used, and this applies particularly to iron, copper, aluminium or tinwares.

To ensure quick dissolving and perfect mixing the solution should be well stirred or shaken. Stirring is best and for small volumes a glass rod may be used. A hardwood stirrer is best for large volumes. The same stirrer should not be used for developer and fixing bath alike; a separate stirring rod should be provided.

#### TAP-WATER

Unless a formula specifically calls for distilled water, the usual domestic supply can be used for almost all photographic solutions and therefore for developers.

Where the water is very hard it can be treated as described on page 92, so that no precipitation of lime salts occurs. If this is not practicable, then the solution should be allowed to settle and the clear supernatant liquor decanted off. This procedure is sufficient in the case of most developers.

Where a perfectly clear developer is essential, filtration is necessary, using a funnel and filter paper or cotton wool. With rather large volumes the funnel and filter paper are too slow and a quick and cheap method is to use filter cloth held in a hardwood frame over the tank which is to hold the developer. The filter cloth must be well washed after use and care must be taken when filtering developer or aerial oxidation may occur.

#### SATURATED SOLUTIONS

A saturated solution is a solution of any chemical which, at a particular temperature, is incapable of dissolving any more

of that chemical. In general, normal room temperature, that is about 68°F. (20°C.), is understood.

The preparation of a saturated solution is a comparatively simple matter and is carried out as follows: The water or other solvent is slightly warmed and the substance to be dissolved is added with constant stirring until no more is dissolved and a residue remains at the bottom of the vessel. That is a sign that the solution is saturated. The solution is now allowed to cool down to room temperature; in doing so a further quantity of the substance will crystallise out. When the solution has reached room temperature it can be filtered or decanted from the residue.

It will be realised that the amount of salt required to saturate a solution is dependent on temperature, but in photography we are only interested in "cold" saturated solutions, that is solutions at room temperature.

#### PERCENTAGE SOLUTIONS

A certain amount of misunderstanding exists in some quarters as to how a solution containing a prescribed percentage of a particular constituent should be prepared.

Suppose we want a 10 per cent solution of potassium bromide: we weigh out 10 parts of the bromide, it may be 100 grains or 10 grams, and we dissolve it, not in the full quantity of water required, but in about three-quarters of the amount. When the bromide is wholly dissolved we then make up the liquid to the correct volume. If we have weighed out 100 grains, then we require 1,000 grains of solution by weight. That is, 2½ ounces within a few minims. If we have taken 10 grams we require exactly 100 millilitres, so as to get a 10 per cent solution by weight. It is quite true that had we dissolved 10 grams of bromide in 100 ml. of water, the error would have been a small one and not of any significance in photographic operations, but we should not have made up an exact 10 per cent solution.

The use of correct weight per cent solutions is particularly helpful when it is desirable to obviate the weighing of numerous very small quantities. It is much easier and quicker to measure out a few minims or a millilitre or so of solution than to weigh a grain or the tenth of a gram, provided always that the photographer uses the metric system. It has to be

admitted and is clear from the following example that when working with the avoirdupois system the use of percentage solution is not quite so convenient.

Suppose we required a solution having the composition

Potassium ferricyanide	100 grains	5 grams
Potassium bromide	30 grains	1.5 grams
Water to make	40 ounces	1000 ml.

If we have stock solutions of 10 per cent potassium ferricyanide and 10 per cent potassium bromide, we make our solution up by taking:

Potassium ferricyanide, 10% solution	2 ounces	50 ml.
Potassium bromide, 10% solution	5 drams	15 ml.
Water to make	40 ounces	1000 ml.

Certain chemicals which keep well in solution can also be kept on the shelves in standard per cent solutions.

#### DILUTE SOLUTIONS

For preparing dilute solutions of known strength from concentrated solutions it is, of course, essential that the percentage content of the concentrated solution be known. If we are working on the metric system using cubic centimetres, the procedure is very simple.

Suppose we want a 10 per cent solution and our concentrated solution contains 40 per cent. We take 10 ml. of the concentrated solution and add water to make the total volume 40 ml., then we have 40 ml. of a 10 per cent solution. If our concentrated solution contained only 32 per cent then we should still take 10 ml. but we should add water to make 32 ml. Hence using metric volumes we take the number of ml.'s representing the percentage we require in the dilute solution and we add water to make up the number of ml. equal to the percentage of the concentrated solution.

With English measures it is not so simple unless we confine our volumes to minims or drams, when we can use the same rule; hence to make a 10 per cent solution from a 40 per cent we should take 10 drams of the 40 per cent

solution and add water to make 40 drams (5 ounces) and so on.

#### WATER UP TO . . .

In many formulae we find the instruction "water up to" or "water to make" and then the required volume is given. This is always a clear direction to dissolve the ingredients called for by the formulae in a lesser volume of water, generally about two-thirds, and then when solution is complete to add further water to bring the whole to the required volume.

As already mentioned, it is often the custom in modern formulae to direct that a certain volume of the water shall be used at a temperature of 120°F. (50°C.). In such formulae the total volume of water required is usually indicated at the bottom of the list of ingredients accompanied by the sentence, "water to make", or sometimes "cold water to make". The meaning of such directions should be quite clear from the above account.

#### WEIGHTS AND MEASURES

Some formulae in this book are given first in English Avoirdupois, and then in the metric system. It is to be noted that the figures in the two systems are not interchangeable, that is to say, a formula must not be compounded by weighing some of the constituents on the English system and some of the metric. The finished solutions, whether made by the English or the metric system, will be similar.

It should also be noted that the English pint, quart and gallon are not the same as the American measures of the same names. The United States' gallon has 128 ounces against the English gallon of 160 ounces. Hence, in the United States, the pint is 16 ounces, the quart is 32 ounces and the gallon is 128 ounces. Whereas in England the pint is 20 ounces, the quart is 40 ounces and the gallon is 160 ounces.

The conversion of British weights and measures to metric, or vice versa, if carried out in the usual way by using exact factors, is a somewhat troublesome procedure owing to the fractions or decimals involved. As a result various conventional conversion factors are employed which, while not

## X.—ENGLISH, AMERICAN AND METRIC EXACT VALUES

### 1.—British Imperial Quart to U.S. Quart

Grains, ounces or pounds per British Imperial quart (40 fluid ounces) multiplied by 0.833 = grains, ounces or pounds per U.S. quart (32 U.S. fluid ounces).

### 2.—British Imperial Quart to Litre

Grains per B.I. quart multiplied by 0.05696 = grams per litre  
 Ounces " " " " by 24.92 = grams per litre  
 Pounds " " " " by 398.7 = grams per litre

### 3.—Litre to British Imperial Quart

Grams per litre multiplied by 17.54 = grains per B.I. quart  
 " " " " by 0.0401 = ounces " " "  
 " " " " by 0.002506 = pounds " " "

### 4.—U.S. Liquid Measure to Litre

Grains per U.S. quart multiplied by 0.06847 = grams per litre  
 Ounces " " " " by 29.96 = grams " " "  
 Pounds " " " " by 479.3 = grams " " "

### 5.—Litre to U.S. Measure

Grams per litre multiplied by 14.6 = grains per U.S. quart  
 " " " " by 0.03338 = ounces " " "  
 " " " " by 0.002086 = pounds " " "

### 6.—British Imperial Liquid Quart to U.S. Liquid Quart

Ounces (fluid) per British Imperial quart multiplied by 0.8 = ounces (fluid) per U.S. quart.

### 7.—British Imperial Liquid Quart to Litre

Ounces (fluid) per British Imperial quart multiplied by 25.00 = millilitres per litre.

### 8.—Litre to British Imperial Liquid Quart

Cubic centimetres per litre multiplied by 0.03999 = ounces (fluid) per British Imperial quart.

### 9.—U.S. Liquid Quart to Litre

Ounces (fluid) per U.S. quart multiplied by 31.25 = millilitres per litre.

### 10.—Litre to U.S. Liquid Quart

Millilitres per litre multiplied by 0.032 = ounces (fluid) per U.S. quart.

## XI.—AVOIRDUPOIS AND METRIC WEIGHT EQUIVALENTS

Pounds	Ounces	Grains	Grams	Kilograms
1.0	16.0	7000.0	453.6	0.4536
0.0625	1.0	437.5	28.35	0.02835
		1.0	0.0648	
	0.03527	15.43	1.0	0.001
2.205	32.27	15430.0	1000.0	1.0



## XII.—BRITISH LIQUID AND METRIC MEASURE EQUIVALENTS

Gallons	Quarts	Fl. Ounces	Fl. Drams	Millilitres	Litres
1.0	4.0	160.0	1280.0	4546.0	4.546
0.25	1.0	40.0	320.0	1136.0	1.136
		1.0	8.0	28.41	0.02841
	0.003125	0.125	1.0	3.551	0.003551
		0.03520	0.2816	1.0	0.001
0.2200	0.8800	35.20	281.6	1000.0	1.0

## XIII.—U.S. LIQUID AND METRIC MEASURE EQUIVALENTS

Gallons	Quarts	Fl. Ounces	Fl. Drams	Millilitres	Litres
1.0	4.0	128.0	1024.0	3785.0	3.785
0.25	1.0	32.0	256.0	946.3	0.9463
		1.0	8.0	29.57	0.02957
0.000975	0.0039	0.125	1.0	3.697	0.003697
		0.03381	0.2705	1.0	0.001
0.2642	1.057	33.81	270.5	1000.0	1.0

exact, are sufficiently correct for all practical purposes. One of these conventions has been used in this book throughout (except in a number of cases where the author of a formula has laid down definite avoirdupois and metric alternatives of his own).

For example, it will be seen that the Avoirdupois ounce is taken as being equivalent to 25 grams and the gram as being equal to 20 grains, whereas their true equivalents are 28.35 grams to the ounce and 15.43 grains to the gram respectively. Although such differences may appear appreciable, in actual practice that is not so because the relative proportions of solid to liquid in the two formulae, that is, in the Avoirdupois and the metric respectively, are much more nearly correct than would appear at first sight, hence the percentage values of the various solutions, when made up in accordance with this convention are sufficiently accurate.

## PH DETERMINATION

In many cases, especially in the processing of colour materials, it is essential to maintain the pH of solutions at its correct value. The simplest method to determine the pH is by the

use of indicators. These are substances which impart to the solution to be tested a colour dependent upon its pH value. For reasonably accurate pH determination, they must show a definite and complete change of colour over a short range of pH. The classical method using litmus paper is for this reason a very unsatisfactory one because this paper changes its colour from red to blue over the comparatively wide pH range from 5.0 to 8.0. Litmus paper should, therefore, only be used to determine roughly whether a solution is acid or alkaline.

#### INDICATOR SOLUTIONS

For the actual pH determination, more sensitive indicators have to be used of which there is a large number available. A considerably shortened list of such indicators, arranged in increasing order of pH is given in the following table.

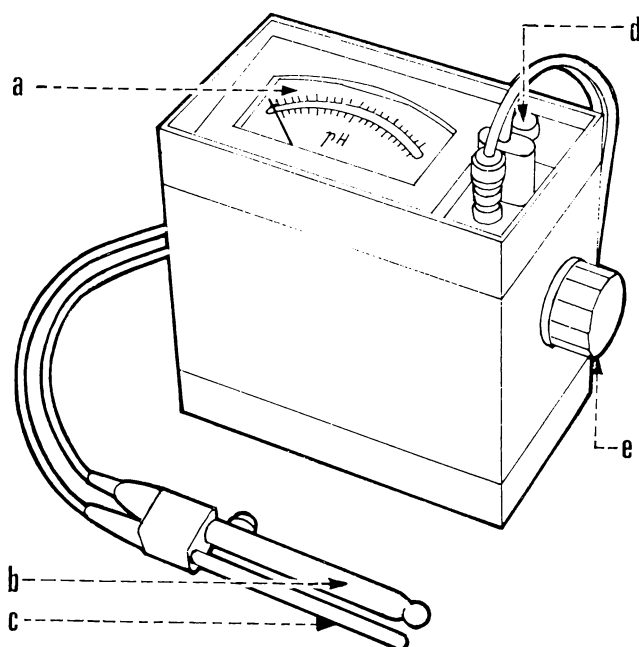
#### XIV.—INDICATORS FOR pH DETERMINATION

<i>Indicator</i>	<i>pH Range</i>	<i>Colour Change</i>
Cresol Red	0.2—1.8	Red to Yellow
Thymol Blue	1.2—2.8	Red to Yellow
Bromophenol Blue	2.8—4.6	Yellow to Violet
Bromo-cresol Green	3.6—5.2	Yellow to Blue
Bromo-cresol Purple	5.2—6.8	Yellow to Violet
Bromo-thymol Blue	6.0—7.6	Yellow to Blue
Phenol Red	6.8—8.4	Yellow to Red
Phenol phthalein	8.3—10.0	Colourless to Violet-Red
Thymol Blue	8.0—9.6	Yellow to Blue
B.D.H. 9011	9.0—11.0	Yellow to Violet-Grey
B.D.H. 1014	10.0—11.0	Green to Brownish-Grey
„	11.0—12.0	Brownish-Grey to Pink
„	12.0—13.0	Pink to Reddish-Orange
„	13.0—14.0	Reddish-Orange to Orange

The approximate pH value of a solution can be determined by using universal indicators. These change colour over the whole spectrum from red to violet within the range pH 3.0 to pH 11.0.

To facilitate the assessment of the correct colour change, an indicator may be used in connection with a series of buffer solutions having known pH values. A given amount of the indicator is added to the test solution and to each buffer, and

## PORTABLE pH METER



An EIL portable pH meter: (a) pH scale, (b) combined glass electrode (pH sensitive) and reference electrode, (c) temperature compensator, (d) set buffer control, and (e) control switch.

## XV.—COLOUR CHANGE OF UNIVERSAL pH INDICATORS

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pH	3.0	red
	4.0	deeper red
	5.0	orange-red
	5.5	orange
	6.0	orange-yellow
	6.5	yellow
7.0—7.5		greenish-yellow
	8.0	green
	8.5	bluish-green
	9.0	greenish-blue
	9.5	blue
	10.0	violet
	10.5	reddish-violet
	11.0	deeper reddish-violet

---

the pH of the test solution is that of the buffer with which it matches. Comparators are also available which largely overcome the necessity for preparing a series of buffer solutions and which simplify correct matching in the case of coloured or clouded test solutions. There are various types of such comparators, some depending on a series of standard buffer tubes, others using permanent colour standards.

### INDICATOR PAPERS

Another simple means of determining the pH value is with the use of indicator papers. The best known material of this type is litmus paper with which however, for the reasons already mentioned, only acid from alkaline solution can be distinguished. Modern test papers cover a much shorter range of pH and are, therefore, more accurate. Most of the indicators in Table XIV are available in the form of indicator papers too and in addition there are special indicator papers prepared from mixed indicators comprising “narrow range” and “wide range” papers. “Narrow range” indicator papers cover the range from pH 2.5-10.0 and the covers are printed in the colours of the papers at intervals of 0.3 pH units. The “wide range” indicator papers carry colour standards for pH values at intervals of approximately 1.0. For the best results, it is advisable to dip the papers into the solution rather than to “spot” the liquid on to the paper.

## **pH METER**

In view of the fact that the change of pH in an aqueous solution is essentially an electro-chemical phenomenon, the determination of pH can be carried out in a very accurate way by direct electrical means. The concentrations of the hydrogen and hydroxyl ions are so related that only one of the two need be determined. The electrical potential between a glass electrode and the solution surrounding it is indicative of the hydrogen ion concentration. In order to measure this potential with a meter, a constant potential reference electrode (calomel) is used to complete the circuit. The meter scale is calibrated in units of pH which is defined as a negative logarithm of the effective hydrogen concentration.

pH meters are available in a large variety of models, either mains or battery operated, all of which are easy to handle and give direct and accurate readings. For the photographic worker a small portable unit will usually be sufficient (see page 117). The process of measuring consists simply of dipping an electrode assembly into the solution and observing the reading on the scale of the instrument after calibration of the meter by dipping the electrodes in buffer solution(s) of known pH value.

The electrode should be treated with great care and never left dry but always dipping in a beaker of distilled water.

## *Arrangement of the Dark-Room*

The fact that the handling of sensitive photographic materials requires a dark room does not mean that any inconvenient corner should be chosen.

Not only should there be sufficient space to work in comfort, but ventilation should be good and the conditions such that even a prolonged spell in the dark-room should be possible without any inconvenience and certainly without any unhealthy influence. Photographic materials are just as sensitive to bad conditions, poor ventilation, damp, etc., as the human organism.

### DARKENING THE ROOM

Darkening the room usually involves dealing with a window, and there is a fairly wide choice of methods. The important point is so to arrange matters so that the window can easily be opened when required.

A very simple arrangement consists of a wooden frame which fits snugly into the window opening, the frame being filled with some opaque substance such as three-ply wood, thick cardboard or even opaque cloth. If the edges require sealing this can be done with adhesive tape.

Where the window is fairly large, a very practical arrangement is one in which the opaque material takes the form of a roller blind running in slits at the side which form an effective light seal. Such frames are not now commercially manufactured but the handyman can make one for himself without much trouble.

The point to remember is that the slides at the side in which the blind runs must be deep enough to form a good light seal. They should be not less than 2 inches deep and about 1/5th inch across, and should be painted matt black

inside. The spring roller blinds can be obtained easily and are built into a partly-enclosed cover at the top of the frame.

## WALLS AND FLOOR

The old idea that the walls of a dark-room should be black or some very dark colour is now dead. Modern darkrooms have light-coloured walls which allow reasonable light in the room. Remember that the walls can only reflect the light which falls upon them: if that light is safe for photographic materials the light they reflect is also safe.

The most serviceable colour for walls is a light grey or even a pure light yellow: the ceiling and, if desired, the upper part of the walls can be finished in white: this is particularly useful when indirect lighting is used (see page 122).

The lower part of the walls should be finished with a waterproof coat which will allow their being wiped down and cleaned with a damp cloth. The area of the wall behind the wet bench where developing and the like is carried out, also behind sinks where they occur should be especially protected against splashes, etc. This can be done either by applying a couple of coats of a good oil paint or by fixing plastic sheeting in such areas. Where a really large volume of work is being done, thin sheet lead is very suitable.

Where rather dim light is much used, as when panchromatic negative material predominates, a useful tip is to paint the corners and edges of tanks, tables, cupboards and the like with white. This renders movement in the dark-room much easier and much more safe.

In a busy dark-room the floor calls for special consideration. It should be protected against moisture and chemical action. The best material is asphalt, or one of the special chemical resistant concrete coatings, but these are expensive and cannot be laid everywhere. The next best is a good quality linoleum which is kept clean and well waxed. This can be underlaid with bitumen paper as an extra precaution against liquids getting through and damaging the actual floor.

## DARK-ROOM ILLUMINATION

The adequate and comfortable handling of a negative material in the dark-room is very largely dependent upon safe and

proper dark-room lighting. The lighting of a photographic dark-room is a compromise between providing illumination of such colour and intensity that the sensitive materials will not be fogged and one which will nevertheless enable the operator to work with minimum inconvenience. It is, therefore, essential that the correct safelight filter is selected and that it is used in a housing of appropriate design and fitted with a bulb of the correct wattage.

*Safelight Filters.* Ordinary blue-sensitive emulsions can be handled in a quite high intensity of red, dark-brown or red-brown light. Orthochromatic materials must be used in a reasonable intensity of dark red light. Panchromatic films are sensitive to all colours and require the use of a light of lower intensity and a dark green filter. These materials are comparatively little sensitive to this colour while the eye is appreciably more sensitive to green than to red particularly at low intensities.

Special filters (see Table XVI), are used for X-ray and infra-red materials. However, in all these cases the sensitive material used must not be exposed to the light for a longer period than necessary nor brought nearer than the minimum recommended distance from the lamp.

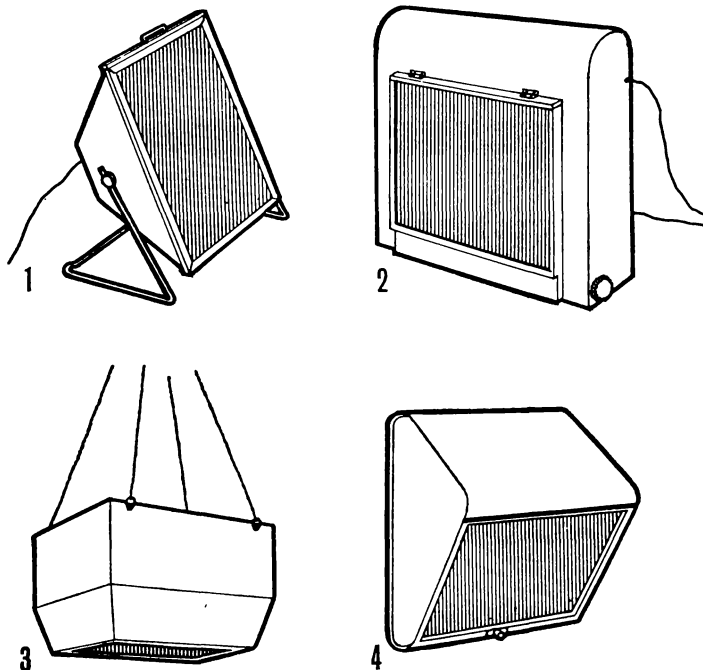
*Dark-Room Lamps.* The actual lighting or illumination of the dark-room depends upon whether it is a small room used only occasionally, or a fairly large room in which developing is being done fairly constantly. For the small dark room direct lighting is sufficient. As a general rule a 25-watt pearl lamp should be chosen and the light source arranged about 4 ft. from the working place. For a larger dark-room where a good volume of work has to be done, indirect lighting will be required as general illumination. The reflecting surface, usually the ceiling, should be smooth and white. If the room is too high or the ceiling otherwise unsuitable, a reflector should be suspended above the lamp.

A suitable set-up is a white ceiling board about 5 ft.  $\times$  4 ft. fixed about 10 ft. from the floor with a ceiling-type dark-room lamp suspended approximately 16 in. below it. A 25-watt pearl bulb should be used.

Material which can be handled by indirect lighting should, nevertheless, not be handled closer than 6 ft.-7 ft. from the reflecting surface.



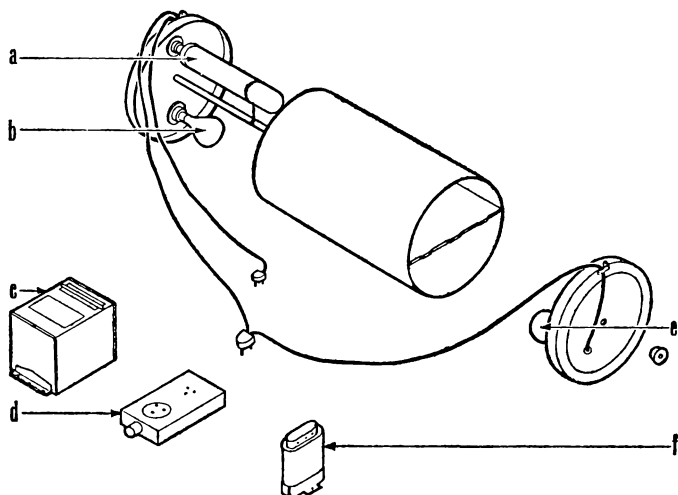
## DARKROOM ILLUMINATION



For the adequate and compatible handling of a negative material, it is essential that the correct safelight filter is selected and used in a housing of appropriate design, fitted with a bulb of the correct wattage.

1. Standard lamp for bench use with 15 or 25 watt bulb. 2. Shelf lamp for wall or bench use with a 40 watt bulb. The safelight may be swung backwards leaving a white glass panel for negative or transparency inspection. 3. Ceiling lamp with two safelights and 15 or 25 watt bulb. Provides both direct and indirect illumination. 4. Lamp for wall fixing to give local illumination with 15 or 25 watt bulb.

## SODIUM SAFE LAMPS



These lamps provide maximum general illumination with adequate safety for low-speed non-colour-sensitive materials. The greatly-increased level of general illumination affords much greater working comfort with very low running cost. The modern type of this lamp does not only contain the sodium tube, but combines it with a tungsten bulb.

(a) A sodium tube, (b) 25-watt tungsten bulb, (c) Leak transformer, (d) Ceiling box, (e) Second 25-watt tungsten bulb, (f) Capacitor.

The pyramid lamp, see page 123, is designed to provide either direct or indirect illumination, as is the very similar beehive lamp. These lamps can be hung from the ceiling or fixed to the wall and can be adjusted to throw the light on the place where it is required. Bulb, 25-watt pearl, distance not closer than 4 ft.

The work-bench lamp is designed to give direct diffused light on to the working place from the wall or shelf or the bench itself. When the lamp is mounted on the wall a space of at least 1 in. must be left to allow a clear passage of air at the back to prevent overheating.

The ceiling lamp of the type shown on page 123 can also be supplied in a model incorporating two safelight filters, one arranged in the bottom of the lamp for direct illumination and one on top of the lamp for indirect illumination. Both filters can be used simultaneously or separately. If both safelamps are used the working distance should be not closer than 4 ft. from the bottom of the lamp (bulb 25-watt pearl).

#### **SODIUM SAFELAMPS**

Sodium safelamps are especially suitable for large printing rooms, not smaller than about 20 × 30 ft. They provide maximum general illumination with adequate safety for low speed non-colour sensitive materials. The design of these lamps is such that the illumination from one sodium safelamp is equal to that of about ten conventional dark-room lamps. The greatly increased level of general illumination affords much greater working comfort with very low running costs.

The modern type of this lamp not only contains the sodium tube, but combines it with a tungsten bulb. Diffusers producing either an amber coloured light or an orange light can be used. The light from one sodium safelamp consumes an average of only 75-95 watts.

The working distance from the lamp should be at least 10 ft. When the lamps are to be used in smaller rooms, it is essential to fit the special neutral density filters provided for these lamps, to reduce the brightness of the light to a safe level. The lamp shown on page 124 is cylindrical in shape, the outside case and the two end pieces being plastic mouldings. One end piece is fitted with two bayonet cap lamp holders for the sodium lamp and a tungsten lamp. The other

## XVI.—SAFELIGHT FILTERS

										<i>Kodak</i>		<i>Ilford</i>		<i>Agfa-Gevaert</i>				
Non-colour sensitive										1	Red	F904	Dark Brown	R1	Red-Brown			
Orthochromatic										2	Dark Red	Iso 906	Dark Red	R3 R4, R5	Red Dark Red			
Panchromatic and some colour films										3	Dark Green	GB 908	Dark Green	G4	Dark Green			
										13	Amber							
X-Ray										6B OC	Brown Amber	X 905	Olive Green	O7	Olive Green			
Intra Red										9	Blue Green	Infra- Red 903	Yellow Green					
										2.5	5	30	30	2.5	10	10	40	0.5

end piece is fitted with one lamp holder for a second tungsten lamp. The lamps are usually suspended in a horizontal position on two chains from the ceiling. The electrical connections from the safelamp are plugged into the sockets of the ceiling box. A special transformer is required suitable for use on 50 cycle AC supplies. Another necessary accessory is a power factor capacitor.

## VENTILATION

Every dark-room should be well ventilated, but the means used to that end will naturally depend upon its size and the volume of work done in it.

In large business establishments an installation is required both to provide fresh air and to exhaust the used air.

In a room of normal size which is reasonably well ventilated when in ordinary use, two openings, one at ground level and one at ceiling level, should provide adequate ventilation. Naturally they must be light tight, but this is not difficult to arrange. The overall size of the openings should be about 6 × 30 in.; the light traps are formed by thin boards providing a double right angle channel which effectually prevents any direct beam of light penetrating. Each light trap must be painted matt black over the whole of the interior. The two wings of the light trap can be about 3 in. apart (see page 131).

## HEATING

Whenever possible it is best to maintain the temperature of the dark-room at approximately 68°F. (20°C.). If central heating or air-conditioning is not available electrical heaters that do not give out any light are recommended, such as oil filled radiators or tubular heaters fitted with thermostatic control. Paraffin and gas heaters should never be used since not only do they emit light but they use up the oxygen of the air and their fumes may affect photographic materials. If the temperature of the dark-room can be kept close to the working temperature thermostatic baths for maintaining the temperature of the processing solutions are not required for small scale processing.

In summer months or in hot climates where the temperature

is likely to be above 68°F. (20°C.) refrigeration units can be used and for the professional or industrial dark-rooms full air-conditioning that ensures adequate temperature control and ventilation is recommended. For the amateur, however, solutions will have to be cooled to the required temperature or shorter development times used (see page 72).

#### LIGHT-TIGHT ENTRANCE

In the case of a busy dark-room where there is much movement of personnel, the entrance should be some form of light trap.

The simplest way is to build a light-tight space into which the door can open, in front of which is hung a heavy light-tight curtain. For large establishments an arrangement with double doors and more space between them is necessary, or the light-tight labyrinth (see page 130).

#### THE WORKING PLACE

As the greater part of the work in a dark-room consists of handling solutions, an ordinary work bench is unsuitable, and in planning a dark-room, provision should be made for tanks or sinks to accommodate the various baths.

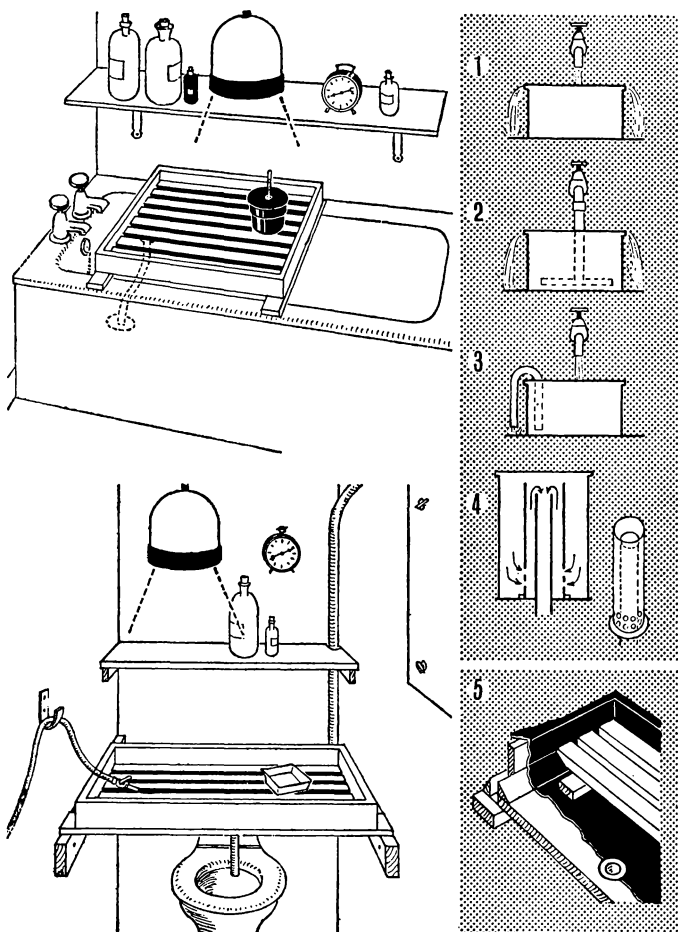
In the small dark-room stoneware sinks can be used, but where a big volume of work has to be handled lead-lined wood troughs or sinks are preferable. A wooden rack should cover the bottom of the sink so that dishes and tanks can stand on it to allow the free flow of liquid through the sink. As an extra precaution against wet floors, etc., the under-part of the tanks can be provided with a separate draining board (see page 130).

In large installations it is usual for the fixed films to be washed in a daylight or otherwise lit room; this involves the provision of a light-tight trap for passing in and out.

#### IMPROVISING A DARK-ROOM

Such arrangements as have just been discussed are not for the amateur, who frequently must make the bathroom his dark-room. In such a case the best arrangement is to have a wooden rack which fits on top of the bath (see page 129).

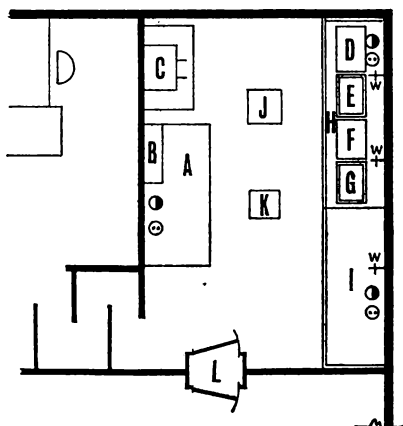
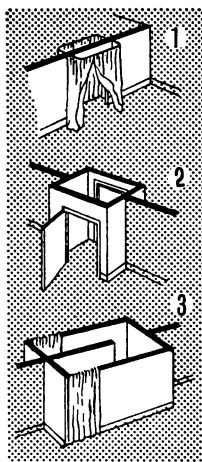
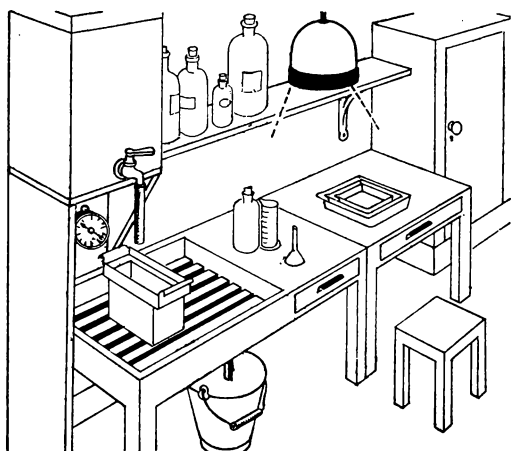
## DARKROOM LAYOUT AND EQUIPMENT



*Left Top and Bottom: TWO IMPROVISED DARK-ROOMS. Right, 1-4: METHODS OF WASHING. Right, 5: MAKING A WOODEN TANK OR SINK*

(See pages 128, 134)

## DARKROOM LAYOUT AND EQUIPMENT



*Top:* DARK-ROOM WITHOUT RUNNING WATER.

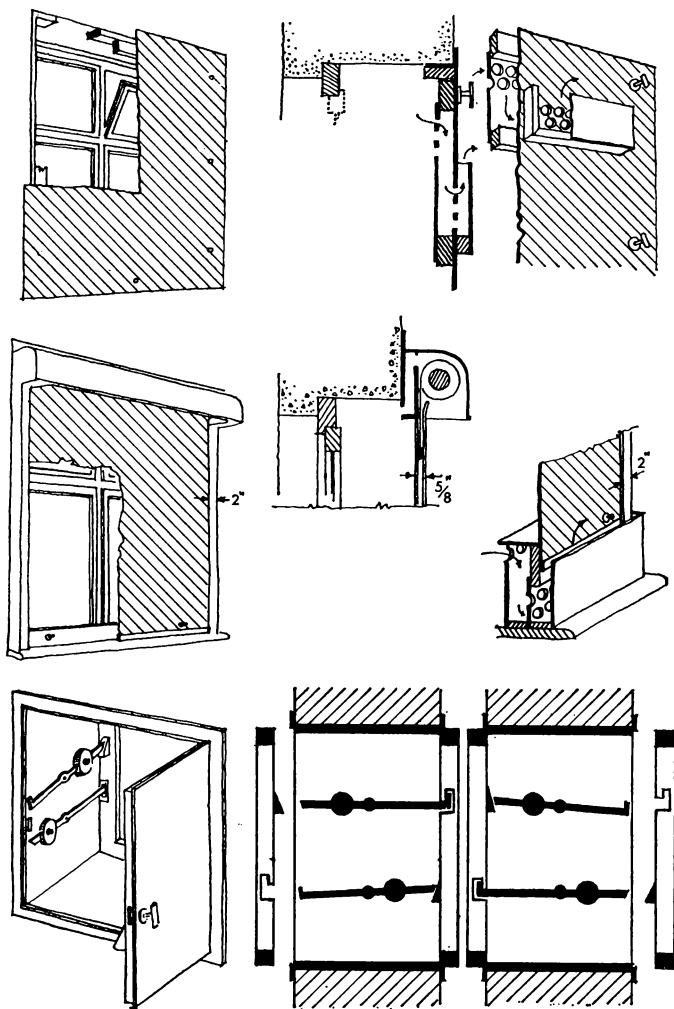
*Right Bottom:* GROUND PLAN OF LARGER DARK-ROOM.

*Left:* ARRANGEMENTS FOR LIGHT-TIGHT ENTRANCE

(See pages 134-135)

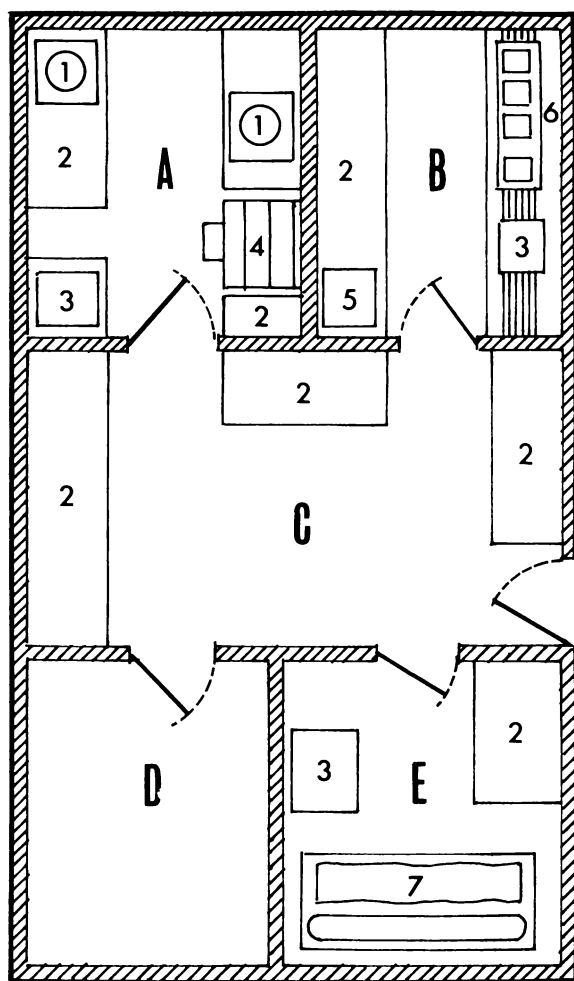


## DARKROOM LAYOUT AND EQUIPMENT



*Top and Centre:* DARKENING WINDOWS AND VENTILATION.  
*Bottom:* LIGHT-TIGHT HATCH WITH SAFETY LOCKING DEVICE  
 (See page 135)

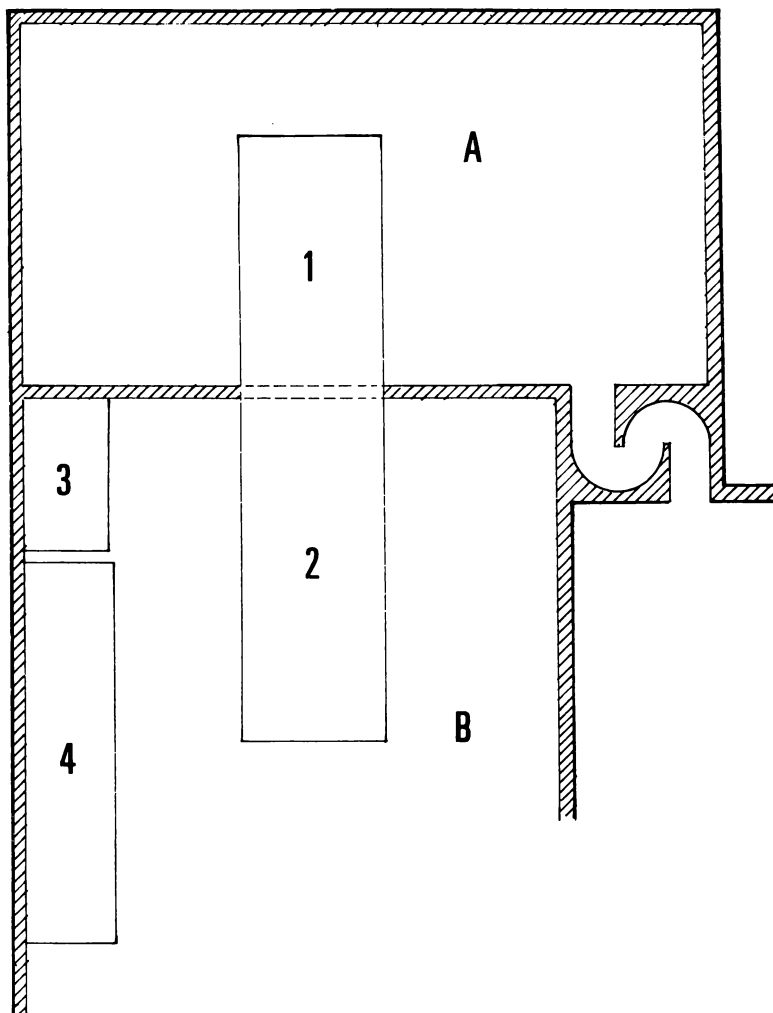
## DARKROOM LAYOUT AND EQUIPMENT



ARRANGEMENT FOR SMALL PROFESSIONAL OR INDUSTRIAL DARKROOM

(See page 136)

## DARKROOM LAYOUT AND EQUIPMENT



ARRANGEMENT FOR A LARGE-SCALE PROCESSING  
MACHINE  
(See page 136)

On this can be placed a large enamelled dish which can be supplied with water through a rubber tube from the tap.

Where a small room is available, then it can be arranged so that everything required in ordinary dark-room work is to hand (see page 130).

When possible, arrangements for drying as well as for printing, enlarging, etc., should be separated from that part of the room where developing and the like is carried out. This can sometimes be done in a simple manner by dividing the room into two by means of a light partition which allows one part to be used in daylight while the other remains the actual dark-room. In such a case only the apparatus which really belongs to the dark-room is kept there; all other operations, including the washing of materials if desired, are then carried out in the other room in which all after-treatment of the negative is done, including reduction or intensification if necessary (see page 130).

**Page 129 IMPROVISED DARK-ROOMS.** The drawing shows a method of improvising a dark-room in a bathroom or even a lavatory. It consists in providing a wooden frame of such dimensions that it can rest on the sides of the bath, or on small supports if a lavatory has to be used. The frame supports either a metal tray or wooden dish which has a drain hole and a rubber tube to carry away waste. The bottom of the tray or dish has a wooden rack upon which dishes or tanks can rest. In the upper drawing a daylight developing tank is shown. In addition to the frame a shelf is provided upon which the necessary additional apparatus can rest, such as a dark-room clock, the safelight, measures, bottles, etc. In the upper drawing a simple dark-room lamp is shown, but below is one with three safelights, yellow, green and red, which are controlled from the switch at the side.

**Page 129 (1-4): RIGHT AND WRONG METHODS OF WASHING.** However washing is done it is essential to remove the used wash water which contains hypo. The hypo left in the emulsion diffuses out into the water in the vessel and remains there unless special measures are taken to remove it. In case 1 this is not achieved; unless the stream of water from the tap is very strong it simply overflows at the sides. The arrangement in 2 is better, where the water flows in at the bottom of the wash vessel; but 3 and 4 are better still, where the water is syphoned away and constantly being renewed by fresh water straight from the tap, so gradually removing all the hypo. In 3 the syphon is fixed at the side of the tank, but in 4 it is built into it and is part of the outflow.

**Page 129 (5): MAKING A WOODEN TANK OR SINK.** The drawing shows how the sink shown on page 125, *left*, can be built in a simple manner using wood. The inside of the tank can be painted with bitumen paint, or lined with thin lead or polythene sheet.

**Page 130 (Top): DARK-ROOM WITHOUT RUNNING WATER.** Many a photographer has to manage without running water. The

drawing shows a good arrangement under such conditions. One-half the working bench or table is made in the form of a sink, which has a drain leading into a bucket. Above the sink, on a bracket, is a water tank. Lighting is by means of a dark-room lamp, hung from the ceiling. The drying rack for plates is on the shelf and a small developing tank is in the sink. Dishes, measure, etc., are on the table.

**Page 130 (Bottom): GROUND PLAN OF LARGER DARK-ROOM FOR BUSINESS PURPOSES.** The main part of the plan shows the arrangement of the dark-room proper with light-tight entrance communicating with the room on the left. A is the general work or sorting table with shelf B. C is the cupboard for the developing hangers, D the developing tank, E the rinsing tank between developing and fixing, F fixing tank and G the washing tank. I is a large sink in which dish development can be carried out. J and K are ceiling safelights and L is a light-tight hatch. Taps, wall safelights, etc., are indicated by easily understood symbols.

**Page 130 (Left): ARRANGEMENTS FOR LIGHT-TIGHT ENTRANCE AND EXIT.** (1) Door with heavy curtains hung either side of the door opening. (2) Small cubicle with double doors. (3) Labyrinth without doors, allowing free ingress and egress, with or without curtains; if the side passage can be made sufficiently long, curtains are not necessary.

**Page 131 (Top): SIMPLE WINDOW SHUTTER OF PLY-WOOD.** A wooden frame is fitted to the window and the sheet of ply-wood screwed to it as shown in *top left-hand* diagram. Ventilation can be assured, as seen in the *top centre* sketch, by means of a row of holes cut in the ply-wood, over which is arranged a small light-lock, the details of which are indicated in the *top centre* and *right-hand* sketches. The holes in the main sheet of ply-wood are protected on the inside by the box-like structure with opening at the top, while on the outer side another similar structure carries a row of holes situated some inches above those in the main sheet of ply-wood, thus providing a light-lock which allows free access of air but prevents any light entering.

**Page 131 (Middle): DARKENING BY ROLLER BLINDS.** The blind runs in slots at either side of the window which provide efficient light-traps. If desired a ventilating trap can be arranged at the bottom of the blind as shown in the sketch on the right-hand side. The arrangement is similar to that described above, and can be at the side or across the whole width of the window as desired.

**Page 131 (Bottom): LIGHT-TIGHT HATCH WITH SAFETY LOCKING DEVICE.** The details can be seen from the three sketches. Two iron levers, each with a weight which normally keeps them in the locked condition, are fitted to the side wall of the hatch. Each door has a countersunk catch into which one end of the levers can fall and also a small ramp set opposite the other lever which prevents it locking so long as the door is open. As soon as one door is opened, thus removing the ramp, the corresponding lever falls by virtue of the weight and so automatically locks the opposite door. When the open door is closed the ramp again comes into action, raising the lever and so releasing the opposite door.

**ARRANGEMENT FOR SMALL PROFESSIONAL OR INDUSTRIAL DARKROOM.** The space is divided into five areas: A. The enlarging room containing enlargers 1, benches 2, a sink 3, and a self-threading roller paper processor 4 (see page 166). B. The black and white negative room containing benches 2, a sink 3, a drying cabinet 5, and a tank processing line 6. This room could contain an automatic processor of the Versamat type (see page 166) if the quantity of black and white negatives to be dealt with justified its use. C. The print finishing area containing large areas of work surfaces 2 for trimming and mounting prints etc., and for carrying out copying work. D. The office. E. The colour processing room containing a bench 2, a sink 3, and a universal tube or drum processor 7 (see pages 169–171) for processing colour negative, reversal and print materials. All rooms are fitted with light-tight doors and the appropriate services including adequate ventilation for the processes and processors being employed.

**ARRANGEMENT FOR A LARGE-SCALE PROCESSING MACHINE.** A. Darkroom area containing the processing part of the machine 1. This area may also contain benches and splicing machines if the processor is a continuous roller processor, or the splicing machines may be placed in an adjoining darkroom not shown in this diagram. B. Light area containing the drying section of the processing machine 2. For ease of operation and control this area also contains the circulating pump units 3 and the replenishing system 4 which for many large machines are not situated alongside the processing tanks. The associated areas where films are received, printed (if a negative process) cut and collated prior to despatch, are not shown in this simplified layout for the processor.

## *Methods and Apparatus*

There is a bewildering choice of possibilities for the development of photographic negative materials. There are hundreds of formulae, dozens of methods and innumerable items of apparatus. The simplest question is which method to employ;

- (1) Dish or tray development.
- (2) A small developing tank.
- (3) Large-tank development.

Which of these methods is the most practical depends upon the character of the negative material and the quantities that have to be handled.

Dish or tray development is suitable for single plates or flat films. Roll film or film for the 35 mm. camera should not be dish developed; such a method is unpractical and will almost certainly result in scratches or streaks along the length of the film. The process also becomes dirty and unpleasant.

The small developing tank is much used today for developing single roll films, including 35 mm. This is generally a small cylindrical tank taking just sufficient developer solution for the correct development of one film. Multiple tanks are also available to take a few films.

For the handling of both plates and films in quantity, large-tank development is now the general rule everywhere, because of the enormous saving in time and money.

### INDIVIDUAL OR TIMED DEVELOPMENT?

In earlier days the question of individual development played a great part in the selection of development methods.

Individual development involved influencing the character of the negative by varying the time of the development at the

desire or caprice of the photographer. This meant that the negative image had to be under observation during the development process, and for this reason dish or tray development was preferred to all other methods. The opposite process was development by time, in which all negatives were developed for a definite time without special control.

It was argued on behalf of individual development that errors of exposure could be corrected and the gradation of the negative controlled to suit the positive material.

In order to see just how far these claims are true, we must examine the possibilities of influencing the negative characteristics in and during development. Is there, in fact, any true foundation for such claims?

We already know (page 35) that time of development has an influence on gradation and density. The longer the development, the steeper the gradation (higher gamma value), until a definite limit is reached (gamma infinity). If we set out the growth of blackening of the negative for different development times in the form of a diagram showing the various steps of blackening as on page 27, we shall reveal the actual character of the development process. We shall see graphically that with increasing time the steps are steeper, but that finally they form a kind of platform (= maximum blackening of the negative), and the density no longer increases.

The possibility of controlling gradation in this manner was of importance in the early days of photography because the photographer had only one type of paper at his disposal, and that paper had only one gradation. In those far-off days, when only albumen paper could be obtained, the photographer aimed at obtaining a negative which would produce a good print on that paper; that meant that he had to produce a negative that was neither too hard nor too soft. Hence when his subject was contrasty he developed for softness by giving a comparatively short development, but when his subject lacked contrast he had to give a long development and to obtain a medium contrast negative. His desire for a developer of a versatile character and for a method which gave reasonable control of the negative is therefore understandable. He preferred to work with a developer which changed its properties on dilution, on variation of the relative quantities of its constituents, and which produced different results according to the time of development applied.



The position of the modern photographer is quite different. He has at his disposal a range of papers of almost infinite variety of contrasts and can therefore produce a good print from any negative whether it be hard or soft in gradation. Moreover, he cannot give individual treatment to a single exposure because his film provides a series of exposures which it is, in general, quite impracticable to handle separately. So, development by time is rarely possible.

The various formulae in this book, when used for the times indicated in each case, produce negatives having the characteristic of a "normal" negative as defined on page 65. Where the negatives are of contrasty objects a soft gradation paper is used, and a hard gradation paper for soft negatives. Hence what the earlier photographer sought to obtain, often unsuccessfully, by manipulating the development process is today more easily and certainly obtained by choosing the right grade of printing or enlarging paper.

#### COMPENSATING DEVELOPMENT

In a somewhat similar manner photographic technology today deals with another question, namely the rectification of errors in exposure. How it does this can be made clear by reference to our density staircase or steps on page 25.

What effect has an error in exposure on the building up of the silver image of our negative? If we give too short an exposure only the lower part of the staircase will be developed; with a longer exposure the scale will be extended towards the upper part.

The great exposure latitude of modern negative material permits so long a tone scale that there is actually room for quite considerable errors of exposure. The actual differences between negatives which have received different exposures is not in gradation, as can be seen on page 37, for the steepness of the steps is the same over the whole range, but in the fact that the densities of the longer exposed negative lie higher up the scale than is the case with short exposures. In printing this means that negatives of short or long exposure can be printed on the same paper, but those with the heavier or higher densities or blackening require a longer exposure in printing as compared to those which have had a short or normal exposure.

We can now ask what effect development time has on the various exposed negatives? If we compare the range of densities of a negative which has had a short development time, with another which has received normal development, we shall see that short development has given us a lower contrast and densities. That means that we must use a contrasty paper for printing and a short exposure. So far as the finished prints are concerned there will be no serious difference between them, and the same will apply in respect of errors of exposure, whatever variations we may adopt in the development process.

In fact, the great exposure latitude of modern sensitive material is sufficient in itself to bridge over errors in exposure in the great majority of cases. There are some special exceptions which we shall discuss in the section dealing with developer formulae (page 172), but as a general rule it will be well to avoid any tricks or special techniques in the actual development.

#### DISH OR TRAY DEVELOPMENT

In early days this was the most widely-used method of development. Today it finds application in the handling of single plates or films. We have already seen that it affords the possibility of observing the growth of the image during development and, to some extent, influencing the process. Let us gather together the various factors that can influence the character of the negative and arrange them as a short set of rules.

- (1) A strongly diluted developer results in a soft negative.
- (2) Increased development time increases contrast.
- (3) The stronger the concentration of the developer the more quickly it will develop, and the more speedily will high contrast be reached.
- (4) With home-compounded developers increasing the alkali content provides a means of accelerating the rate of development and therefore contrast. This procedure requires great care, otherwise there is the danger that fog will be produced.

The way in which the properties of a developer can be varied by altering its composition is shown in Table XVII.

The table shows how it is possible to obtain nine variants of this particular developer, so that almost every type of result from a very soft to a hard gradation can be obtained.

A dash in the table denotes no change in the standard formula under the particular heading of the column.

It will be seen that in No. 1 the hydroquinone content is 60 grains (3 grams) and the soda is 2 ounces (50 grams) and a very soft working developer is obtained. No. 2 is somewhat more contrasty as only the hydroquinone is altered; in No. 3 the hydroquinone is increased to 100 grains (5 grams) and the soda content is as in No. 1.

In No. 4, the higher hydroquinone content results in more brilliant, that is somewhat harder, results. In the variations 5-9 the chemical composition of the developer is not altered but the degree of dilution is varied and so an increasing degree of brilliance or hardness is attained.

#### XVII.—VARYING OF FOCAL UNIVERSAL M.Q. DEVELOPER 16

Effect	Quantity of Hydroquinone	Quantity of Alkali	Degree of Dilution	Minutes of Developing
Soft	1 60 grains or 3 grams	2 ounces or 50 grams	1 : 7	5
	2 80 grains or 4 grams	—	1 : 7	5
	3 100 grains or 5 grams	2 ounces or 50 grams	1 : 5	5
Normal	4 100 grains or 5 grams	—	1 : 5	5
	5 —	—	1 : 10	5-6
	6 —	—	1 : 7	6-7
	7 —	—	1 : 5	7
Hard	8 —	—	1 : 1-2	4-5
	9 —	—	Undiluted	3-4

The temperature of the developer is very important, and it should be kept at 68°F. (20°C.) as it greatly affects the development process.

A low temperature slows down development and hinders the building up of density, while a high temperature accelerates the process and introduces the additional danger of fogging.

Dishes or trays for developing are made of plastic, glass,

porcelain or stainless steel and should be rigorously reserved for their special purpose. They should never be used for other photographic purposes such as fixing, for which separate vessels should be provided. If the dishes in use are of the same size and material they should be marked with a waterproof paint, D for developing, F for fixing, so that there shall be no confusion and no mixing of dishes. Metal dishes or tanks other than of stainless steel must be coated with a good chemical (preferably rubber based) paint for protection.

Plates or films for development are laid into the dish sensitive face upward, and care must be taken to ensure that the developer flows evenly and quickly over the whole of the surface. This is best achieved by tilting the dish slightly so that the solution accumulates at the lower end, then placing the plate or film in the dish, quickly lowering the raised end so that a wave of developer flows quickly but smoothly over the whole of the plate or film surface. A little wetting agent added to the developer will avoid the risk of air bubbles sticking to the surface of the emulsion and retarding or even preventing development in those areas.

The dish should be kept in gentle movement, by rocking, during the whole time of development to ensure even action of the developer. This is particularly important in view of the retarding effect of potassium bromide (see page 91), which can accumulate locally in the developing film and cause uneven development if the developer does not flow freely over the developing surface.

One can now observe the beginning and the progress of the development process, and if the necessity arises, make such corrections as seem called for. In the normal handling of negatives we may meet with the three following possibilities: (1) Correct exposure. (2) Under-exposure. (3) Over-exposure.

(1) *Correct Exposure.* As we shall see later (see page 231), the appearance of the first trace of the image and the way in which the image builds up varies somewhat with different developers, but the normal order of appearance and development is as follows.

The first to appear are the highlights, those parts of the subject photographed which were most brilliantly lit; next come the well-lit parts, then the half tones and finally the details of the shadows, that is, the darkest or least lit portion of the picture.

The density and gradation of the negative can be roughly judged by looking at the back of the plate or film and choosing the right moment for stopping the development process, that is, the moment that it has reached the desired character. If the negative appears too soft or thin, development is continued until every important detail in the picture is visible. If greater contrast is required, then the time of development will be increased until it is obtained.

(2) *Under-Exposure*. This is shown during development by the appearance of the highlights, then much more slowly the other details and the half tones appear, but the details in the shadows refuse to appear even after excessively long development.

A badly under-exposed negative cannot be saved by any manipulation of the developer. Those parts of it which received no exposure or an insufficient amount cannot be developed, for there is nothing there to develop. It is therefore quite wrong in such a case to attempt the use of a concentrated developer, the effect of which will be to exaggerate the contrast of that part of the image which has developed without in any way improving the rendering of shadow detail.

The old-fashioned remedy of diluting the developer is equally fruitless, for there is nothing in the negative to be saved. At the best all that we can do is to make use of some method of after-treatment (see page 339), or choose a more suitable grade of printing paper.

(3) *Over-Exposure*. This shows itself in development by the whole image flashing up quickly, and not merely the high lights: that is always an indication of over-exposure.

It is not an indication to stop development; on the contrary, the process should be continued until the negative is fully developed right through. True, the image will be dense and the whole negative dark but, thanks to the latitude of modern materials, the gradation will be a usable one. If the development be stopped too soon the negative will be too flat.

#### JUDGING THE NEGATIVE

It must be accepted that a certain amount of experience is necessary in order to judge correctly the character of a

negative during development. The creamy silver bromide in the film is deceptive and appears to increase the covering power of the developed silver. When a negative has been fixed and the undeveloped silver bromide removed, the negative looks much less dense than it did before, and appears to have "gone back" or retrogressed. Hence the old and well-known rule that the negative examined by the dark-room light must always appear somewhat denser than is actually required in its finished state.

Owing to the high general and colour sensitivity of modern materials, the negative should never be exposed for any length of time to the dark-room light. A short glimpse should suffice to indicate the nature of the control required. Although we speak of safelights, the term is a relative one and even the safest red light can fog an orthochromatic film if it is exposed long enough.

With panchromatic materials control is difficult, even with a green safelight. The usual green safelight prescribed gives sufficient illumination to enable one to move about the dark-room in safety, and to see where apparatus is, but not sufficient to allow judging a negative.

Hence for panchromatic material either time development should be used (see page 38), or a desensitiser employed (see page 251).

The emulsion layer on plates or films is very easily damaged, either mechanically or chemically, at every stage of the photographic process. It should be a rule never to touch the emulsion surface with the fingers; a glass negative should always be held by the edges—if it is a small one, then the thumb and forefinger should suffice and only the edges of the negative need be touched. Flat film or roll film negatives must be held by an edge which is free from any image.

If the face of an undeveloped plate or film is touched there is always the danger of markings being caused either through the natural oiliness of the skin, perspiration or plain dirt or dust. In any case there is likely to be some interference with the process of development.

Even after processing and drying the emulsion can easily be marked and spoiled by being touched with moist or dirty fingers and such markings are particularly troublesome when enlargements have to be made.

## SMALL TANKS

The difficulty of developing a long length of film in a dish has already been mentioned, and although special long narrow dishes were once produced for the purpose of developing films, they did not prove popular. In addition, the modern fine-grain developers call for a comparatively long development time, and if the dish or developer container is to be kept in constant movement while development is taking place, a great deal of time is lost.

For similar reasons the drum-type of developing machine did not achieve any great amount of popularity. It consisted of a glass drum or barrel mounted on metal bearings. Under the drum was a dish which contained the developer solution. The film was threaded on the drum and as this revolved so the film, passing through the developer, was developed. The drum had to be kept in movement during the whole of the process, and one real disadvantage was that for much of the time the developing film was exposed to air which gave rise to a number of troubles of which aerial fog was only one. The drum idea has been revived for processing and details of modern drum and tube processing are described on page 170.

A notable solution of the whole problem lies in the many small developing tanks which have been evolved. The essential principle of these is that the film is developed whilst wound up in spiral form, and that only sufficient solution is required to develop a single film. The film is wound in spiral form, in which it occupies minimum space, but the conditions must be such that the turns of the film do not touch one another and that the developing solution has free access to the front of the films.

In practice this is achieved in two different ways: by means of an apron or band which serves to keep the turns of the film separate, or by a spiral lead in and guide attached to the central bobbin.

*The apron or band type.* This was the earliest on the market. The film and the apron or band are wound up together on the centre spool of the tank. The apron, which generally consists of celluloid, has projections on its surface which serve to support both the front and the back of the film to be developed, and also ensure the necessary space for the flow of the developer; the apron is often perforated

to help in this direction. The tank itself is usually made of plastic and has a light-tight lid or cover (see pages 147-148).

*The spiral guide type.* Here the apron or band is dispensed with, and the film is held in position during development by spiral leads or guides forming part of the central bobbin. Small projections occur at regular intervals round the inside of the spirals and so hold the film in position, and also allow free circulation of the developer. This principle permits of universal tanks which can be used for the development of films of various sizes: to this end the spiral guides are made adjustable and can be fixed in any desired position on the centre axle (see page 148). Modern tanks of this type are frequently constructed of stainless steel which makes them more robust and easier to clean than plastic tanks.

The capacity of the smallest of such tanks is about 11 ounces (300 ml.), but those for miniature films take a much smaller quantity and are therefore very economical.

The loading of the tank must be done in the dark-room, but once the light-tight cover has been put on, the rest of the procedure can be carried out in daylight.

Most models are supplied with inlet and overflow so that the film can be rinsed with water when development is completed, and then the fixing solution introduced without necessity of opening the tank or using the dark-room.

Certain types are available which actually permit the loading operation to be carried out in daylight, and so dispense with the dark-room altogether. The idea is alluring, but it has to be admitted that these tanks are not so simple to operate, are somewhat less safe and are distinctly more expensive (see page 149).

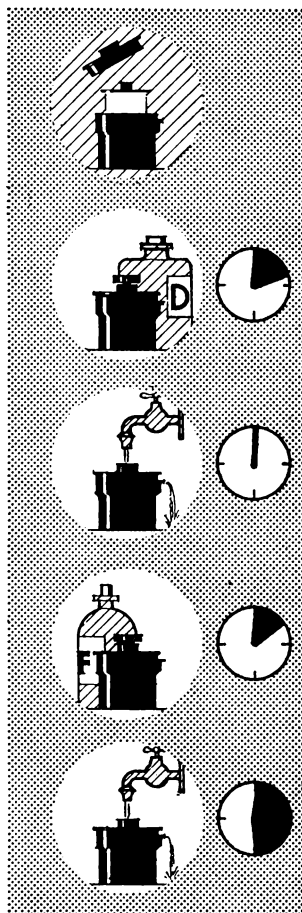
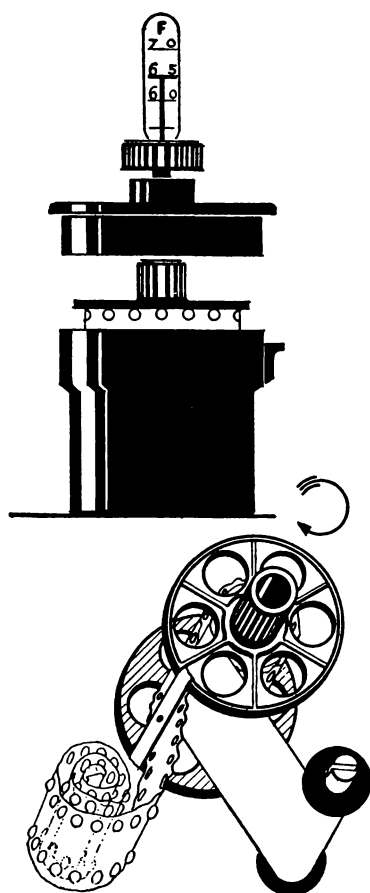
The usual procedure is to place the loaded spiral in the tank and then pour in the developer. With modern, fast-pouring tanks, this is usually quite safe. If development time is at all short, however, it is advisable to fill the tank first and lower the spiral gently into the developer.

Precautions must be taken against the formation of air bubbles and their attendant dangers. Many developers now, however, contain a wetting agent to obviate this problem. Nevertheless, it is a sensible precaution to disperse any bubbles that may have formed by giving the tank a short but fairly strong shake just as development begins.

It is not convenient to maintain the tank in constant move-

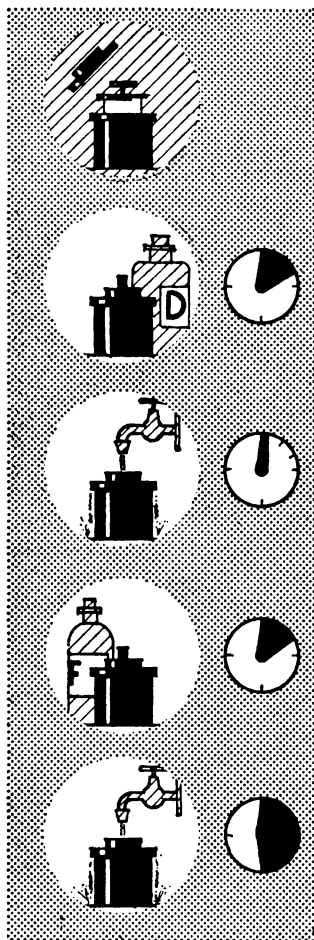
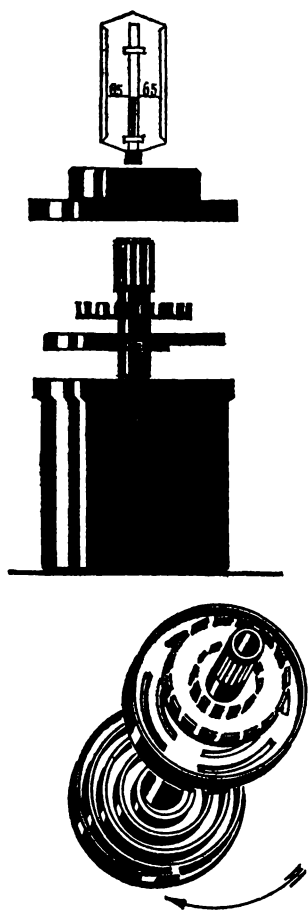


# DEVELOPING TANK, APRON TYPE



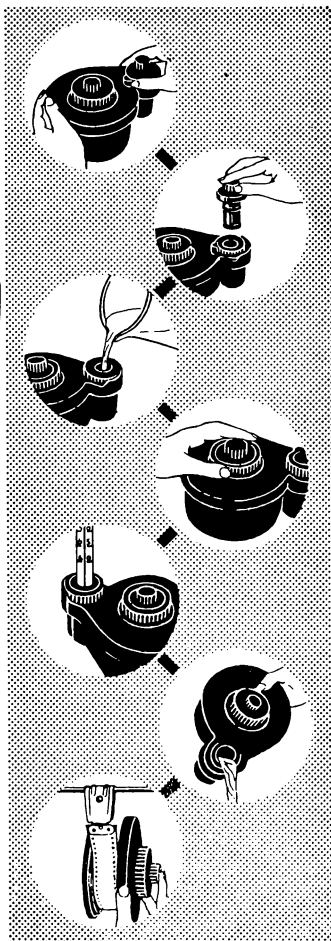
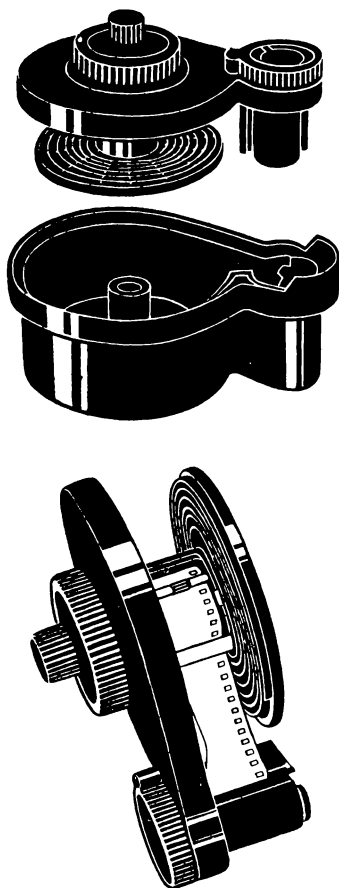
(See page 151)

## DEVELOPING TANKS, SPIRAL GUIDE



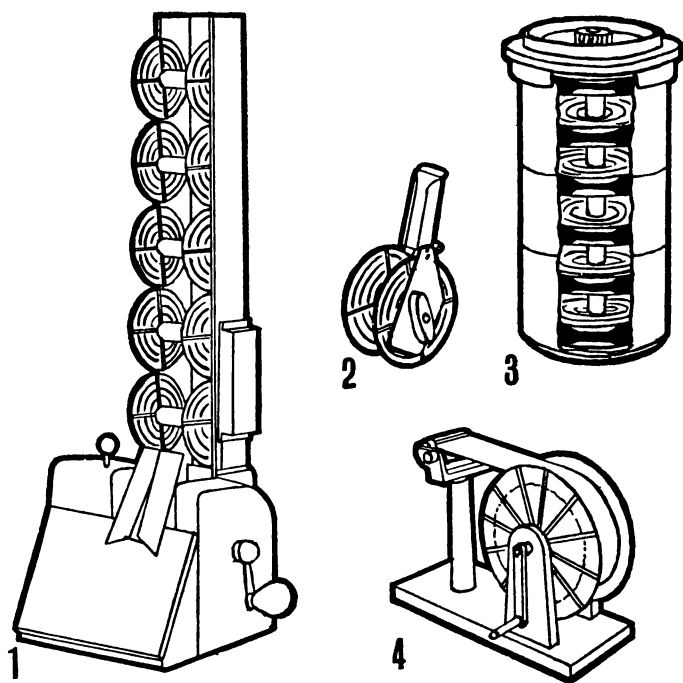
(See page 151)

## DAYLIGHT-LOADING TANK



(See page 151)

## LOADING OF SPIRALS



Development in spiral spool tanks is a well-proved method, but has always been subject to some practical difficulty in loading the spools particularly when using longer films or when a larger number of spools is to be used. These difficulties can be overcome by mechanical guides which feed the film automatically into grooves from the centre outwards.

1. Machine for loading spools automatically. 2. Device for threading film into the spiral by hand. 3. Multiple-storey tank containing five spools. 4. Loader for longer length of film.

ment during development, but a certain amount of agitation is essential. In many cases this is brought about by revolving and/or raising and lowering the spiral by means of a rod projecting through the lid of the tank. Most modern tanks are spill-proof and can be completely inverted. If neither is possible, then the tank must be gently shaken to and fro. Whichever form of agitation is used, it should be carried out at regular intervals throughout development.

There exists apparatus which automatically agitates the spool, either by means of a small water turbine or a tiny electric motor driving a small pulley on the spool, the connection being made by a rubber band. The cost of such a device is, however, somewhat high and, as a result, such mechanical agitation has not been widely adopted.

Page 147: DEVELOPING TANK, APRON OR BAND TYPE. *Left top*: the complete apparatus—thermometer, knob for agitating film during development, cover, spool and tank. *Left bottom*: method of spooling with film and apron, the backing paper being previously removed. *Right from top to bottom*: processes of development: (1) The spool is placed in the tank in the dark-room. (2) When the developer has been added and the cover closed, the tank can be brought into bright light and development proceeded with. (3) The developer is poured away and a short rinse given. (4) The fixing bath is introduced and 10 minutes fixing given. (5) Washing for 30 minutes follows the fixing.

Page 148: DEVELOPING TANK, SPIRAL GUIDE TYPE. *Left top*: the assembling of the tank. *Left bottom*: spool with spiral guide for the film. The film is wound on to the spool after the backing paper has been removed. *Right from top to bottom*: steps in the process: (1) Placing the film in the tank in the dark-room. (2) Development. (3) Rinse between development and fixation. (4) Fixation. (5) Washing. The last three processes can be carried out in daylight.

Page 149: DAYLIGHT-LOADING DEVELOPING TANK. This particular model is designed for daylight processing of 35 mm. black-and-white film when it is in standard 35 mm. cassettes. To use the tank, the film leader must extend outside the film cassette. The film can then be loaded, developed, rinsed, fixed and washed in the tank in daylight. The tank has two chambers, into one of which the cassette of film to be developed is wound before development. To load the tank, the cover is raised as shown in the top drawing on the left. The film cassette is inserted into the cassette chamber and the film leader threaded into the spiral as shown in the bottom drawing on the left. The cover is replaced on the tank and the film wound from the cassette on to the tank reel by turning the reel collar. Now the cassette collar is rotated (first drawing on the right) to cut off the film from the spool by means of a stationary knife located within the tank. By lifting out the cassette knob the empty cassette can be removed (second drawing on the right). The developer is poured into the opening at the top of the cassette chamber and the film agitated during development by rotating the reel collar (fourth drawing). The

temperature can be measured during development by inserting a thermometer into the magazine chamber. After development is complete, the developer is poured out, the tank filled with water for rinsing and then with fixing bath. To dry the film, fasten the end, while it is still on the reel, with a film clip suspended from the ceiling or a shelf and unwind the film as shown in the last drawing on the right.

#### RAPID DAYLIGHT PROCESSING OF 35 mm. FILM

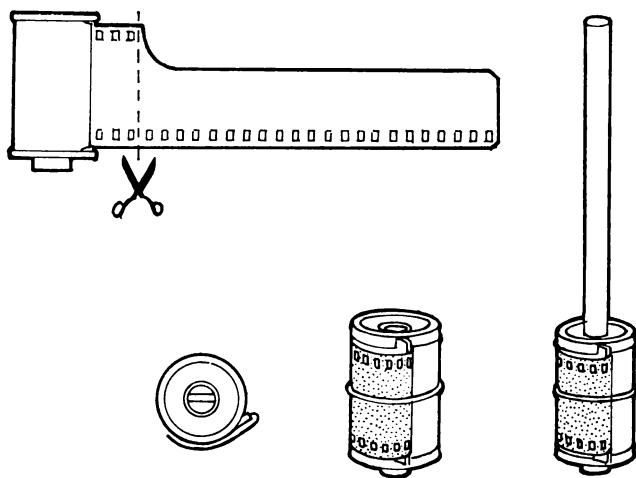
A very simple procedure for the rapid processing of 35 mm. film in the cassette has been described by Kodak Ltd. The procedure requires that a twenty exposure 35 mm. film be given only sixteen exposures: two extra blank exposures should be made at the beginning of the film and two more at the end. It is also important to ensure that after the sixteen exposures have been made the film leader is not re-wound into the cassette, this can best be achieved by taping the leader to the take-up spool when loading the film into the camera.

The apparatus required is a small beaker or measure, an agitation rod approximately six inches long that fits tightly into the cassette spool and a monobath solution (see page 153).

Processing is as follows:

- (1) Cut the leader from the film leaving approximately one inch of film protruding from the cassette as shown in the top diagram on page 153.
- (2) Wrap the protruding film back around the cassette and secure with a rubber band as shown in the bottom diagrams on page 153.
- (3) Insert an agitation rod into the cassette and rotate *gently* to tighten the film on the cassette spool.
- (4) Slowly unwind the film by rotating the agitation rod anti-clockwise counting the number of turns until resistance is felt.
- (5) *Slowly* lower the cassette into a measure or beaker containing sufficient monobath solution (see page 153) to cover the cassette whilst winding and unwinding the film by the number of turns determined in step (4). Carry out this winding and unwinding procedure twice whilst lowering the cassette into the monobath.
- (6) When the cassette is fully immersed wind the film by half the number of turns originally determined in step (4) and during the recommended processing

## RAPID DAYLIGHT PROCESSING OF 35 mm. FILM



Preparing a 35 mm., 20-exposure film for development within the cassette. *Top:* Removal of the film loader. *Bottom, left to right:* Wrapping the film around the cassette, securing the film with a rubber band, and insertion of the agitation rod.

time (about 3-8 minutes depending on the film and monobath used) rotate the rod to and fro through about one and a half turns.

- (7) After processing lift the cassette and allow the monobath solution to drain, discard the monobath solution and immerse the cassette in water of approximately the same temperature as the monobath. Remove the film from the cassette and wash and dry the film in the normal manner.

The winding and unwinding operations should be carried out gently, making sure that the film is not wound too tightly on the spool; otherwise, scratches may result. It is quite normal for air bubbles to be released from the cassette during processing.

Generally too much rotation of the agitation rod during processing causes dark bands to be formed across the width of the film, while light bands across the width of the film are caused by insufficient agitation during processing.

#### LARGE TANK DEVELOPMENT

Tank development renders possible the development of a large number of films simultaneously. It is therefore essential for the mass handling of negative material and is of particular importance for the photo-finisher.

An intermediate step between the small spiral tank and the large photo-finisher tank is supplied by tanks with a capacity of about three gallons. Spirals are used too but they are placed in baskets (see page 157) making it possible to develop 18-24 films at the same time. To keep the processing solution at the correct temperature these tanks can be placed in a water bath as shown on page 156. Instead of moving the films manually from tank to tank there are processors available where the timing, transporting, agitation and washing is carried out automatically (see page 163). The processing cycle can be programmed and it is thus possible to use the same machine for different processes.

For large scale production deep tanks are used, big enough to accommodate all sizes of roll films fully extended. There are three different types:

- (1) Developer tanks equipped with a circulating pump unit which includes motor and pump as well as the heating



and cooling arrangements, this is mounted at the side of the tank (see page 158). In this way, the space in the tank itself is reserved entirely for the films and the temperature of the solution can be controlled during development without sacrificing tank capacity.

The heating element and the cooling coil are located in the path of the circulating developer so that an even temperature is maintained throughout the tank. For smaller tanks and lower output an immersion heater can be used.

(2) Chemical tanks for the processing solutions in which agitation and temperature control are not so important. All the tanks have grooves on top for supporting the frames and an outlet for emptying the tanks quickly and completely.

(3) Washing tanks used for rinsing the film thoroughly between the individual baths and at the end of development. Fresh water enters through a jet at the bottom of the tank and causes a turbulence in the tank. The used water flows off over the top of the tank.

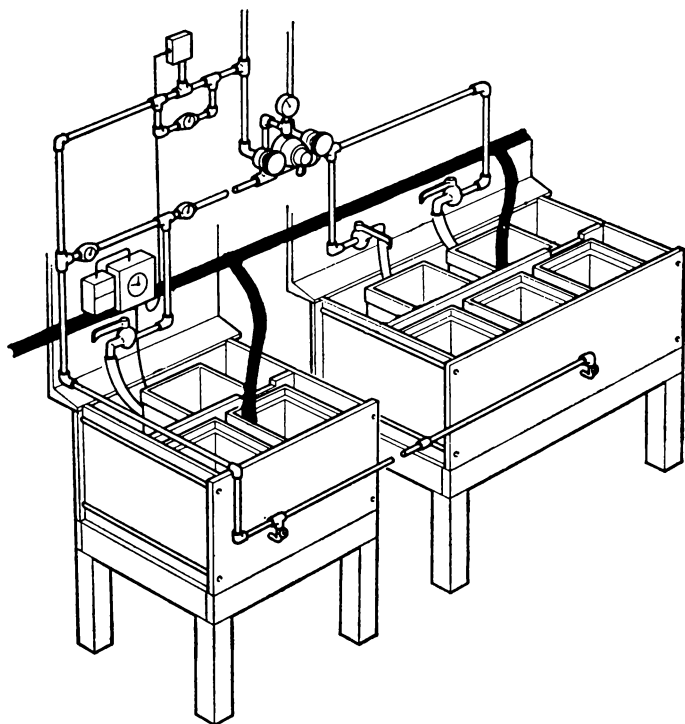
#### AUTOMATIC PROCESSING MACHINES

For large scale processing the movement of films from tank to tank by hand would be much too slow a procedure. Film processing machines are used that transport the films automatically. There are two general types in use, these are *dunking machines* and *continuous processors*.

In dunking machines (see page 161) the films are loaded on bars or racks that grip them firmly, preventing touching or movement, and facilitate quick handling. Sheet films are inserted into special frames. The frames are then lowered into the tank and given one or two sharp up and down movements in order to displace any air bubbles which may have formed on the film surface. The films must not be left in any processing solution without some form of agitation during the time of immersion. The processing tanks are provided with circulating pumps to continuously agitate the solution.

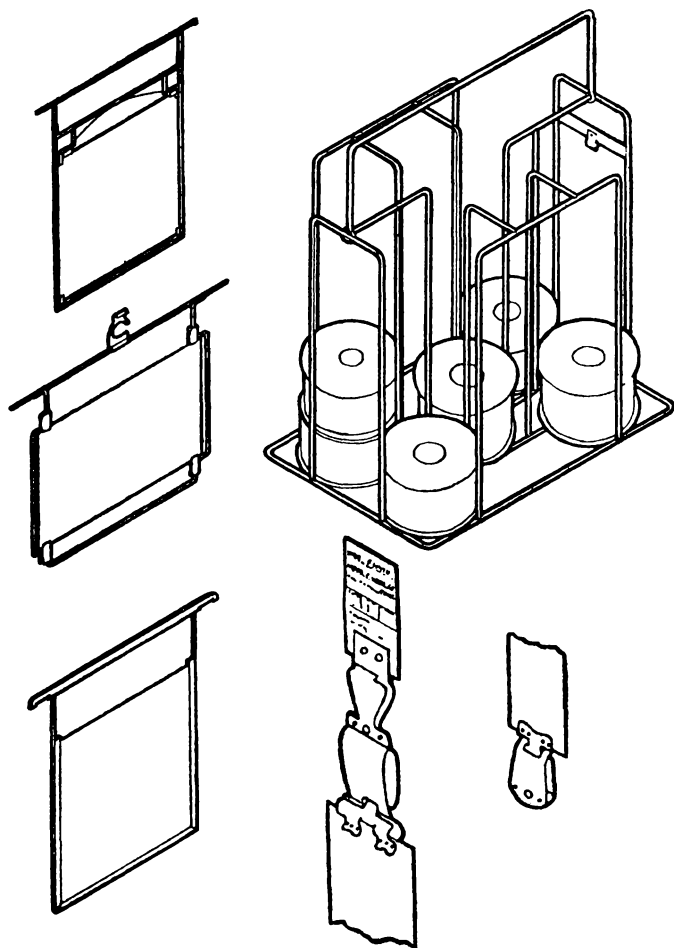
Roller processors transport the films through the tanks by means of rollers that guide the film in and out of the tanks in a sinusoidal path. These machines are of two basic types: *continuous roller processors* (see page 165) which require the films, all of the same width, to be spliced into long lengths

## PROCESSING BENCH



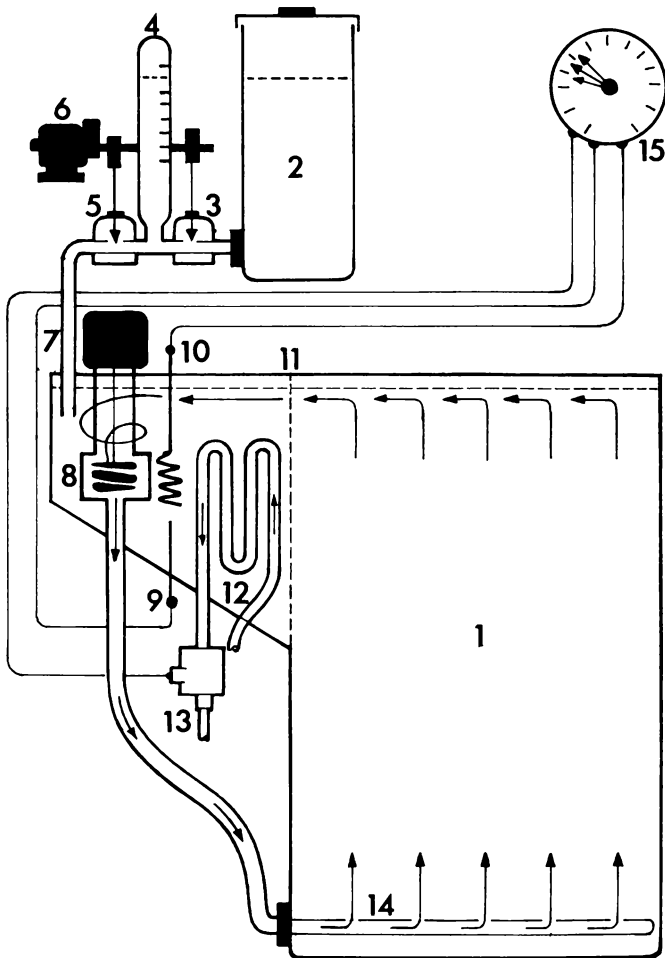
The tanks are placed in a water bath which keeps them at the correct temperature. The bench is also equipped with a unit for nitrogen burst agitation. These processing benches are useful for small scale production in tanks of 3 gallons capacity.

## ACCESSORIES FOR TANK DEVELOPER



To accommodate films and sheet films in small and large tanks, some special accessories are necessary such as baskets for spirals (*top right*), sheet film holders (*left*), clips for roll films (*bottom right*).

## PROCESSING TANKS



For large scale production, deep tanks are used: 1, Processing tank. 2, Storage tank. 3, 4, 5 and 6, Replenishment unit inlet valve, measure, outlet valve, and motor. 7, Feed pipe. 8, Immersion pump. 9, Thermometer probe. 10, Immersion heater. 11, Plate filter. 12, Cooling coil. 13, Cooling water valve. 14, Distribution pipe. 15, Thermometer/thermostat control.

before processing, and *self-threading roller processors* (see page 167 where individual roll or sheet films of differing widths are guided through the various processing solutions and make their own way to the end of the process.

Timing, temperature control, agitation, solution circulation, and in most cases filtration of solutions are all carried out automatically.

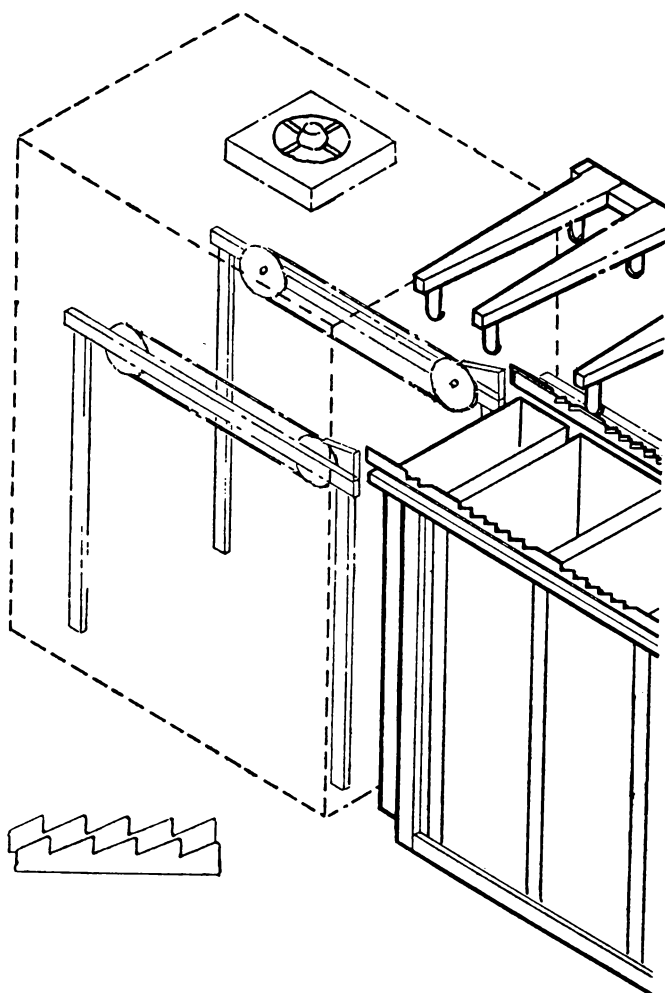
**Temperature Control.** It is of the utmost importance for large-scale processing that the temperature of the solutions, especially the developer, is carefully controlled. This can be achieved either by using a water bath or water jacket for the solution tanks or by controlling the solution temperature itself. When only small quantities of photographic materials have to be processed, manual adjustment of temperature is practicable. An immersion heater either in the water bath or in the solution itself may be sufficient but for more accurate requirements it should be connected with at least a simple thermostat.

When appreciable quantities of films must be handled on a production basis a more accurate and dependable temperature control system is necessary. Thermostatically-controlled mixing valves provide a compact and economical system for the control of water temperatures. These valves operate by mixing warm and cold water to obtain the desired temperature within about  $\pm\frac{1}{2}^{\circ}\text{F}$ . The temperature of the cold water supplied must of course be lower than the temperature required for the mixture. In areas where the cold water during summer months is warmer than the desired temperature, an auxiliary cooling system is necessary.

The water bath or jacket system is usually used for smaller tanks. Larger developer tanks (see page 158) are usually connected with a second tank as shown in the drawing. This tank contains the immersion heater and sometimes a cooling coil and thermostat. The developer solution is circulated by a pump and is thus kept at the correct temperature. At the same time this system provides the necessary agitation for the solution.

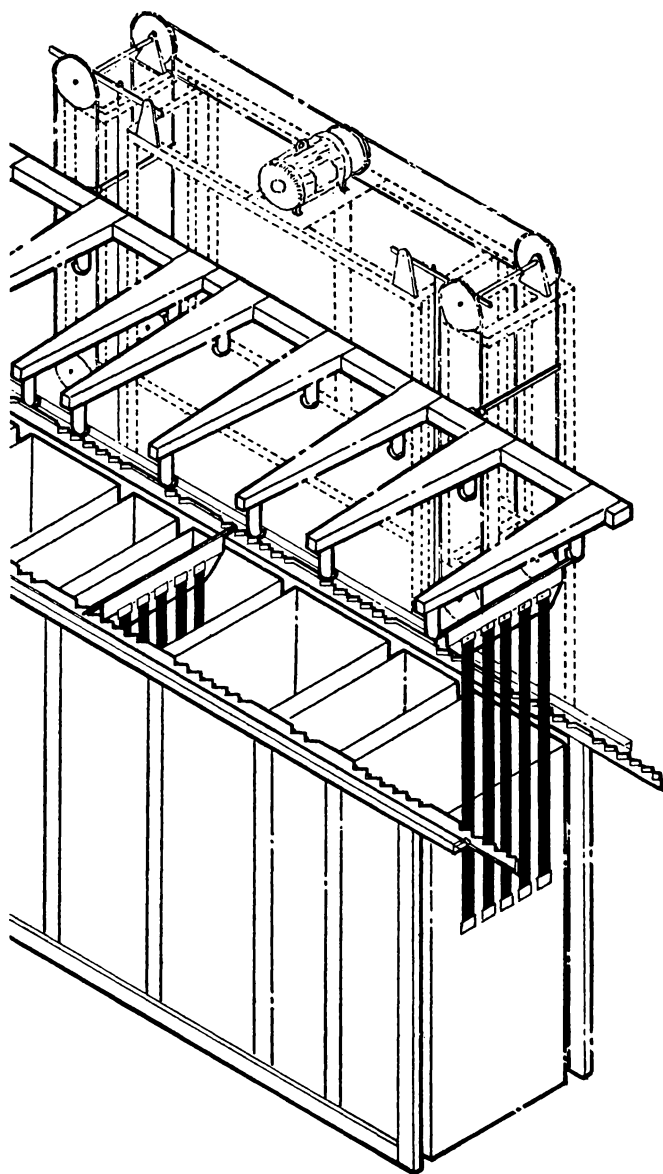
**Agitation by Nitrogen.** Agitation of developer solution can be provided either by mechanical devices such as pumps and propeller stirrers or by gaseous bursts of nitrogen. The nitrogen gas is released very near the bottom of the tank intermittently and provides a consistent and reliable agitation

## AUTOMATIC PROCESSING

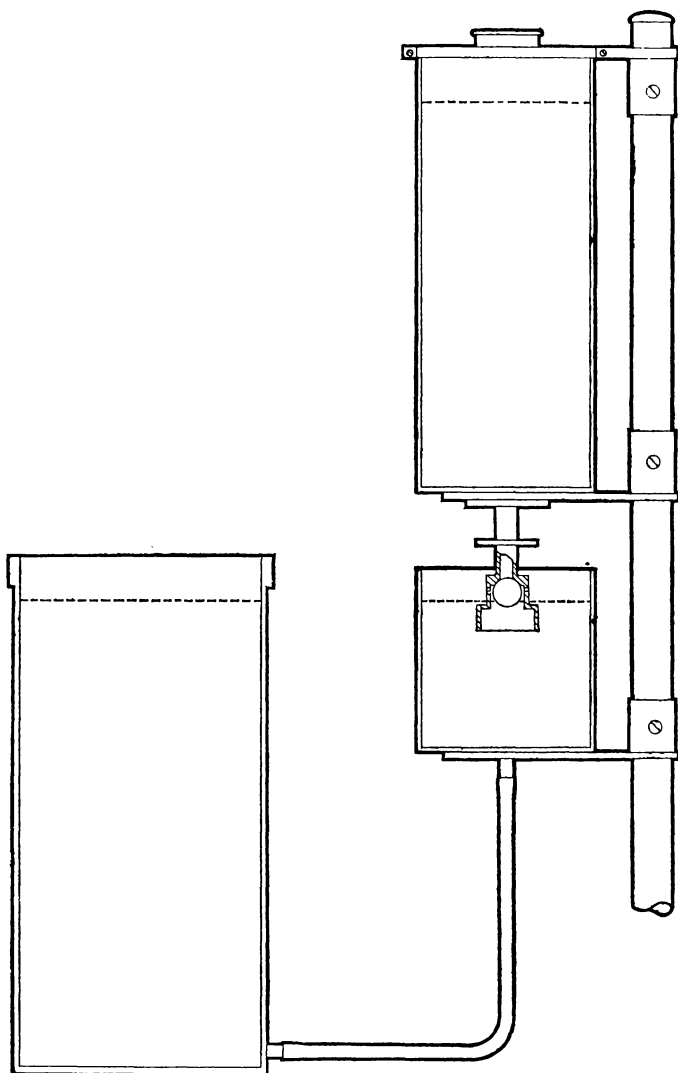


For large scale production, the movement of the frames from tank to tank by hand would be much too slow a procedure and therefore film processing machines are used. Film processing machines do this job automatically. The films are put into clips and hung on bars and are then passed through the machine automatically. The bars holding the films are moved up and down by a chain drive and the films moved forward in each tank by a rack. After washing, they pass through a drying tunnel and are taken out ready for printing.

## MACHINE FOR ROLL FILMS



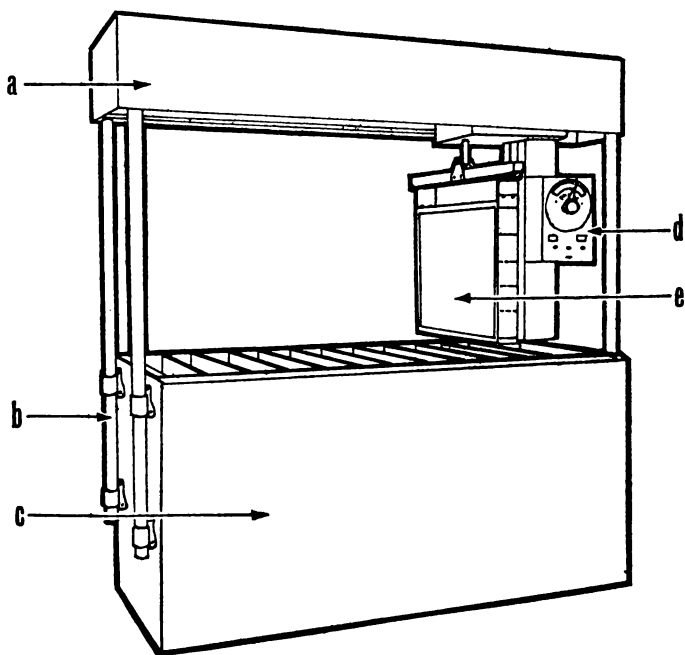
## REPLENISHING UNIT



These units are used to replenish automatically the processing solution in film processors. When the level in the developer tank drops, the ball of the non-return valve falls away, allowing sufficient developer to flow.



## AUTOMATIC PROCESSOR FOR SHEET FILM



Instead of moving sheet film from tank to tank by hand, these machines do this job automatically.

(a) Track for automatic carriages. (b) Tubular support for overhead track. (c) Stainless steel tanks with water jacket. (d) External control panel for programming the machine. (e) Stainless steel basket or rack for film.

of processing solution. To provide automatic control of the flow of nitrogen to the processing tank, an electrically operated solenoid valve is required in the line between the gas pressure reducing valve and the point of release in the tank. The burst valve works usually in conjunction with the burst valve control unit which enables both the duration of the gas flow and the interval between each burst to be regulated within wide limits.

To ensure that all parts of the solution receive equal agitation and that the processing will be consistent, a uniform pattern of nitrogen bubbles is necessary. A special gas distributor is therefore used. It consists of a rectangular grid of plastic tube which is perforated with evenly spaced holes and is connected to the outlet side of the burst valve. The grid rests on the bottom of the processing tank and the tank is carefully levelled so that the pattern of bubbles rises uniformly through the solution and is not concentrated to one side of the tank only. Where the volume of work is large a separate gas distributor for each processing solution is desirable. Each distributor is then connected up to a multiple-outlet manifold at the outlet side of the burst valve. The use of agitation by nitrogen gas is essential for colour development where manual systems of agitation are time-consuming and wasteful of manpower.

#### DUNKING MACHINES

The films are put into clips and hung on bars, or into carriers, and then are passed through the machine automatically. The bars holding the films (see page 160) are moved up and down and the films move forward in each tank by a rack. After washing they pass through a drying tunnel and are taken out ready for printing.

The level and the working strength of all processing solutions are maintained automatically by a replenishing unit such as the one shown on page 162. This unit is made of plastic and has a total capacity of  $1\frac{3}{4}$  gallons, enough to maintain constant level in a 48 gallon developer tank for about three hours continuous working. The container is fed through a  $\frac{3}{4}$  in. diameter pipe into a cup connected independently by rubber tubing to the bottom of the developer tank. The cup is set vertically in a position coinciding with the correct level required in the developer tank. The pipe through

which the developer passes into the cup is fitted with a non-return ball valve to prevent the developer in the tank from rising into the container. When the level in the developer tank drops the ball falls away and allows sufficient developer to flow into the cup and from there into the developer tank.

#### CONTINUOUS ROLLER PROCESSES

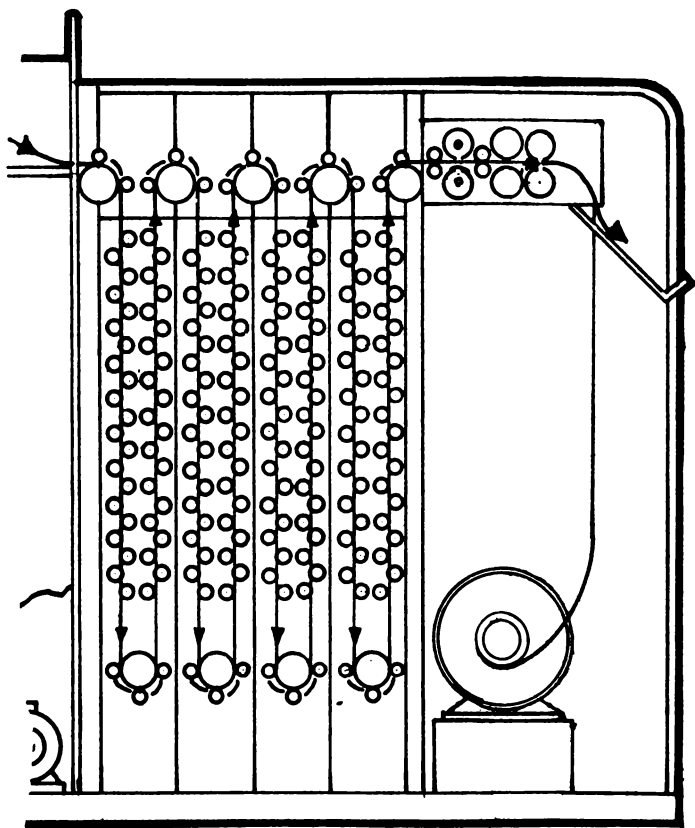
For large scale processing of films of one format, from 16 mm. microfilm to 70 mm. film, the films may be spliced together to form one continuous roll before passing through the processor. The film is then threaded through the machine under light tension between top and bottom rollers of racks in the processing tanks, either in a sinusoidal or helical path.

Normally these processors are threaded with a leader to which the film is joined, and the leader is left in the machine between processing runs to avoid the time-consuming operation of re-threading.

In some machines the film is driven around the rack rollers by means of the film sprocket holes (*positive drive*) and sprocketed drive-rollers at the tops of the racks. The bottom rollers are weighted or spring loaded. This type of drive is used extensively for processing ciné film but is not often used by photofinishers. The reason being that the large number of splices needed are difficult to align accurately, and the inclusion of sprocket holes in the splices is a further complication. Also it is possible that films received by the photofinisher may have damaged sprocket holes due to faulty camera loading or camera film transport.

The machines used by many photofinishers have *friction drives* in which specially constructed rollers, using friction, grip the edges of the film. Film tension through the machine has to be controlled and a means of varying the tension independently is provided in each tank. This is necessary because films expand and contract on going through the various processing solutions. One method of controlling tension is to use a flanged top roller which is free to pivot on a spring-loaded arm. The flange of the top roller can come into contact with a continuously rotating drive roller and so transfer the drive to this flanged roller and then to the film. Thus as tension builds up in one section of the machine, the flanged roller is

## SELF THREADING ROLLER PROCESSOR



The film is transported through the various stages of processing and drying by powered transporting rollers. This system differs radically from conventional hand or machine processing methods. Film hangers are eliminated. The exposed sheet or roll films are hand fed, one at a time, into the feeding tray. The films are then transported by a system of rollers through the processing tanks and drying compartment to the delivery bin. The temperature of the developer is controlled by circulating the solution through a heat exchanger and filter, and by a thermostatically controlled immersion heater in the developing tank. The temperature of the wash water is regulated by a thermostatically controlled mixing valve. The machine also incorporates an automatic replenishing system.

pulled into contact with the drive roller and more film is fed into this section of the machine. This reduces tension to a normal operating level, which allows the flanged roller to be released from the drive roller.

At the output end of the machine there is a *pacer* roller that positively governs the speed of the film through the processor. The diameters of the rollers at the tops of the tanks are chosen so that, when they are turning, slightly more film is fed through the machine than is needed by the pacer roller. This causes the film loops to become slightly slack and the flanged film rollers move away from the drive rollers. The resulting build-up in film tension once again brings them into contact with the drive rollers. The net outcome is a continuous oscillating of the top pivoted rollers as they come in and out of contact with the drive rollers.

#### **SELF-THREADING ROLLER-PROCESSORS**

In these machines the film is transported through the various stages of processing and drying by powered transport rollers. A commercially available sheet film processor of this type is shown on page 166 (Versamat type).

The part of this machine to the left of the panel is the film-feed section normally located in a photographic darkroom. The rest of the machine, consisting of the processing section and the dryer, is located in fully illuminated space on the opposite side of the darkroom wall. To prevent light fog, the developer and the stopbath sections of the processor are shielded by a protective cover.

In normal operation, individual sheets of exposed film are fed singly through a narrow slot in the housing of the feed section. The film is picked up by rollers and delivered to the processing section of the machine where it is accepted by a special grouping of rollers which directs the leading edge vertically downward. The film is then transported vertically in this case at the rate of 5 feet per minute, between driven rollers arranged in staggered positions. Each side of the film thereby receives identical processing treatment. The Versamat type processor can process film at rates up to 25 ft. per minute.

On reaching the bottom of the developer rack, the film is caused to reverse its direction by an arrangement of rollers which has become known as a "turn-around". This device consists of a large driven roller around which are positioned

three smaller rollers and two guide shoes. The shoes and the small rollers, known as "cluster rollers", cause the film to turn 180° around the large or "master" roller, after which it continues vertically upward between the staggered rollers which form the opposite side of the rack.

On reaching the top of the rack, the film enters an arrangement of rollers and shoes very similar to that used in the "turn-around" just described, but inverted to cause the film to leave in a downward direction, and offset, with regard to the developer rack, to cause the film to pass on to the stop-bath rack. When so used, these rollers make up what is known as a "cross-over".

The processing section has four stages: developer, stop bath, fixer, and wash. The processing racks and cross-overs used in each of these positions are substantially identical. In each case, the solution on the film surface is displaced by the action of the rollers in contact with the film and is replaced by relatively fresh solution from the larger volume in the tank. This action provides substantial agitation at the film surface, resulting in uniformity of development and permitting rapid completion of the action of each of the solutions in this case, 60 sec. in each solution.

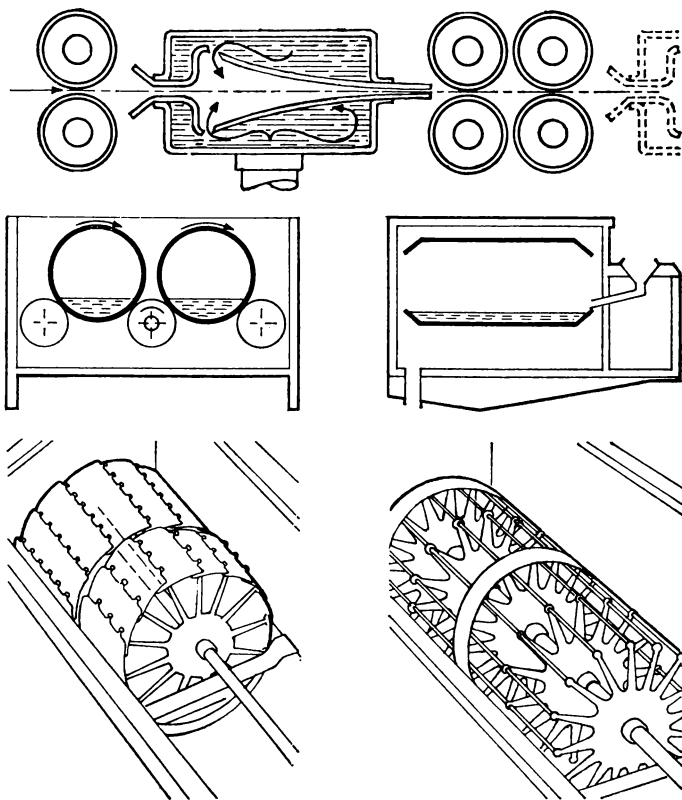
Control of temperature and uniformity of chemical composition throughout the system are maintained by recirculating each of the processing solutions continuously through a system of heat exchangers in which the water used for tempering purposes is finally delivered to the wash tank. In the developer recirculation system, a thermostatically controlled electrical heater is provided to increase the flexibility of the system. In addition, the developer is filtered continuously by being recirculated through a replaceable cartridge-type filter.

Replenisher solution is delivered to each of the processing systems by means of a pump which operates only while film is being fed into the machine. Thus, by controlling the rate of flow through the pump, the solutions are replenished at a rate that is directly proportional to the film load.

After being transported through the wash rack, the film enters a special "exit cross-over", which causes it to turn 90° and delivers it horizontally to the dryer.

On entering the dryer, the film first passes through a pair of powered, soft-rubber wringer rollers which effectively

## PROCESSORS



*Top:* ITEK TRANSFLO SYSTEM. Film is transported horizontally by rollers through the applicators into which the processing solutions are pumped. Slits in the applicators direct a uniform liquid cushion across the film so assisting its passage through the applicator.

The film is dried by a high velocity warm air dryer before collection at the end of the process.

*Centre:* MERZ-TYPE TUBE PROCESSOR. The diagram shows the tubes, drive rollers and constant temperature cabinet.

*Bottom:* COLENTA-TYPE PROCESSOR. On the left-hand side cut film holders are shown and on the right-hand side roll film holders are shown.

remove all remaining surface water. It then passes on to powered transport rollers which carry the film through the remainder of the dryer.

Between each pair of transport rollers and located above and below the film plane are the air-distributor tubes with slit orifices through which high-velocity hot air is directed at both sides of the film.

The commonly used roller processors described above, all use a vertical up and down means of transporting the material through the various processing baths. However, a novel *horizontal* transport of the material is used in the Itek Transflo system (Rolor Co., Syosset, New York). In this "straight-line" transport of the film, deep vertical tanks and large numbers of rollers are eliminated.

The processing solutions are applied to the material by pumping into shaped applicators placed between rollers, as shown in the diagram on page 169. The applicators are designed so that the solution flows across the width of the film and assists the travel of the material. Solutions are returned by gravity flow to the tanks where they are filtered, replenished and maintained at the correct temperature.

It is claimed that this type of processor eliminates phenomena such as "bromide drag" and adjacency effects because of the efficient agitation by pumping of solutions through the applicators. Also the air-exposed "turn-around" rollers are eliminated (a possible source of contamination in the previously described self-threading roller processors). The rollers in these processors operate under compression and act as solution barriers and squeegees as well as transporting the film. For very large-scale operation *roller processors* are used. These contain fewer rollers than the self-threading roller processors and require a leader to be threaded through to which continuous rolls of spliced film are attached.

#### TUBE AND DRUM PROCESSORS

These processors use the "one-shot" system. Small quantities of fresh processing solutions are used for each batch of material and then discarded. This method of processing gives uniform results because fresh solutions are used and no complicated replenishing systems are required. It is especially suitable for photographers who wish to process a large variety



of materials as tube processors are suitable for processing most types of colour or black and white positives, negatives or papers.

The operation of the processors is simple and only the loading of the tube requires to be carried out in the dark. The tubes are surrounded by a light-tight box containing air thermostatted at the required temperature and agitation is accomplished by rotation of the tubes.

The (Merz-type) processor consists of two horizontal tubes in which films or papers are placed. Small quantities of processing solutions or water are then introduced by the inlet funnel and at the end of each stage the tubes are tilted to discard the chemicals (see centre diagram page 169).

Tube processors are available in varying degrees of sophistication from the very simple Merz S30 which has a single tube into which solutions are introduced by pouring into the inlet funnel, to more sophisticated systems which use a pump for introduction of solutions and programming of the processing sequence by a timing clock (such as the "Atmac" processors, Atlas Photography Ltd., London) or even by a punched card (such as the "Atmac" processors or "Colenta" processors, Huss Labortechnik, Weiskirchen). The "Colenta" system uses a drum around which the material is placed emulsion side outwards and processing solutions are pumped into a trough in which the drum rotates (see bottom diagram page 169).

A large variety of drums or processing reels are available for these types of processors for processing most sizes of sheet films, roll films and papers.

Another type of tube processor uses a vertical tube and a novel agitation system (Colorapid, Croydon). Solutions are pumped into the vertical tube containing up to ten 35 mm. film spirals which rotate backward and forward while the processing solution is pumped up and down within the tube. The processing sequence is controlled by a punched program card. This type of machine may be used either for one-shot processing or for a fully replenished system. Like other tube processors it is very versatile and can process most types of colour materials in most sizes depending on the types of tubes used, numbers of reservoirs and programs selected.

## *Developer Formulae*

There are so many developer formulae that it is no easy matter to survey them clearly or to reduce the host of recipes and processes to a definite order. They are, therefore, organized here according to the purpose for which they are designed. The largest group includes the general purpose M.Q. developers designed for universal use. There is then a group of special M.Q. developers to which belong tank, fine grain, high contrast, rapid, tropical and other more specialised formulae.

By far the largest number of modern developer formulae are based on the use of metol and hydroquinone, in some cases replaced by the combination Phenidone-hydroquinone. However, for some purposes, special developing agents are still being used and they are classified here in a separate group.

When interpreting a formula, or designing a new one, or adapting an existing one to a new purpose, we have to consider the photographic effect of the components in the light of the knowledge we have gained from pages 80-105. The main points to keep in mind are these:

- (1) The developing agent, its nature, concentration and, in cases where several are used, the ratio between them.
- (2) The alkali or accelerator, its nature and concentration.
- (3) The preservative, which has, however, only a limited effect on the result.
- (4) The restrainer, its choice and quantity.
- (5) The total concentration of all components.

In tables of developer formulae in which no units are stated, the quantities given are proportions which should be construed as grams for solids and millilitres (ml.) for liquids.

## GENERAL PURPOSE DEVELOPERS

The developer formulae classified in this group, are based on the use of metol and hydroquinone. The main characteristics of these two agents are, as we already know: *Metol*—soft and rapid working. *Hydroquinone*—contrasty and slow working.

By mixing these two ingredients in different ratios and concentrations it is possible to design formulae for nearly any purpose. The other components of the developer, especially its alkali contents must be adjusted accordingly.

The general purpose developers are very versatile and of universal application and by the simple method of diluting a stock solution in different degrees the result can be altered to quite an extent. Even so, it is not possible to alter the contrast of the negative in a degree sufficient for all purposes. There are, therefore, three different types of general-purpose developer, namely:

Group I. Soft Working Developers (Table XVIII).

Group II. Normal Developers (Table XIX).

Group III. Contrast Developers (Table XX).

**XVIII.—GENERAL PURPOSE M.Q. DEVELOPERS**  
*Group I—Soft*

	1 D165	2 ID3	3 G215	4 G212	5 AN40
Metol	6	6	4	2	0.8
Sodium sulphite anhyd.	25	25	25	25	45
Hydroquinone	—	—	—	1.5	1.2
Sodium carbonate anhyd.	37	37	10	25	65
Potassium bromide	1	2	0.5	0.5	1.5
Special additions	—	—	—	—	Pot. metabi- sulphite
Water to	1000	1000	1000	1000	1000
Dilution	1 : 3	1 : 3	none	none	none
Development Time (min)	10	12	5-8½	5	15

**XIX.—GENERAL PURPOSE M.Q. DEVELOPERS**  
*Group II—Normal*

	6 D61a	7 G214	8 AN47	9 AG46	10 AN61
Metol	3	2	1.5	1.1	1
Sodium sulphite anhyd.	90	25	45	21.5	15
Hydroquinone	6	3	3	1.6	2
Sodium carbonate anhyd.	11	16	5	6	15
Potassium bromide	2	1	0.8	0.4	1
Sodium metabisulphite	2	—	1	0.4	—
Water to	1000	1000	1000	1000	1000
Dilution	1 : 1 1 : 3	none	none 1 : 1	none	none
Development Time (min.)	7 * 14	4-8	5-7 12-16	8-10	4-6

**XX.—GENERAL PURPOSE M.Q. DEVELOPERS**  
*Group III—Contrasty*

	11 D11	12 ID2	13 AN30	14 G201	15 D72	16 Focal Universal
Metol	1	2	3.5	1.5	3.1	3
Sodium sulphite anhyd.	75	75	60	50	45	75
Hydroquinone	9	8	9	6	12	11
Sodium carbonate anhyd.	25	37.5	34	32	67.5	75
Potassium bromide	5	2	2	2	1.9	1
Water to	1000	1000	1000	1000	1000	1000
Dilution	none	1 : 2 1 : 5	none	none 1 : 3	1 : 1-2 (see p. 141)	
Development Time (min.)	8	5 9	6	5 10	4 (see p. 141)	

**XXI.—GENERAL PURPOSE M.Q. DEVELOPERS**  
*Two Solution Formulae*

	17 M.Q. I	18 M.Q. II	19 Metol	20 Hydro- quinone
<i>Solution A</i>				
Metol	10	3.5	10	—
Sodium sulphite anhyd.	25	35	50	100
Hydroquinone	—	6.5	—	25
Potassium bromide	—	2.5	—	—
Potassium carbonate	25	—	—	—
Water to	1000	1000	1000	1000
<i>Solution B</i>				
Sodium sulphite anhyd.	25	—	—	—
Hydroquinone	10	—	—	—
Potassium carbonate	25	125	45	50
Potassium bromide	1	—	1	—
Water to	1000	1000	1000	1000
Working Solution	1 part A + 0.5 parts B + water to make 6-12 parts	3 parts A + 1 part B + 4-6 parts water	1 part A + 1 part B	1 part A + 5 parts B
Development Time (min.)	3-5	5	3-5	5-7

Let us look first at Group I—Soft Working Developers, represented by Formulae 1-5, in Table XVIII.

These formulae make use of the soft working characteristics of metol and, as a matter of fact, Formulae 1-3 contains metol only and no hydroquinone at all. Formulae 4, 5 do contain some hydroquinone—about the same amount as or a little more than the metol. The sulphite content of all these formulae is practically the same and is so chosen that the solution has good keeping properties. As alkali, sodium carbonate is used in an average quantity. The alkali content

of the developer must naturally not be too high or it would interfere with its soft-working characteristics.

The next large group (II) contains the normal developers. Their main characteristic is that they use, of course, both developing agents but more hydroquinone than metol. As far as the contents of preservative and alkali is concerned, the same is true as for Group I.

For Group III (Contrasty developers) still more use has been made of the contrasty working characteristics of hydroquinone. In these developers the metol content has been reduced and that of hydroquinone considerably increased. They contain 3, 4 and in one case even 9 times more hydroquinone than metol. The percentage of alkali is normal and in some cases rather high and the sodium sulphite concentration has been increased accordingly to achieve better keeping properties. In general they are also used at less dilution than the developers of the other two groups to get more contrasty results. It should also be noticed that the potassium bromide content is, on average, higher so the developer is more energetic and has therefore a higher tendency to fog.

As these formulae show, the photographic result can be controlled to a wide degree by the ratio of metol and hydroquinone. It naturally occurs to us, therefore, to make up such developers in the form of two stock solutions, one containing metol and the other hydroquinone and to mix these two solutions in the required ratio (Formulae 17-20).

There are other variations of such two-solution formulae. The developers are made up in two solutions, one containing the developing agent or agents and the other the alkali. By increasing the quantity of the second solution higher contrast and rapidity can be obtained (Formulae 131-134).

An example of a developer which can be adapted to a lot of uses simply by dilution, is the Focal Universal Developer (Formula 16).

(1) Undiluted, it is rapid working and contrasty and can be used for technical photography, X-ray films and process work where the highest contrast is not required. Development time 3-5 minutes.

(2) For dish development of plates and films dilute according to the contrast required with from three to seven volumes of water. The more concentrated the developer the higher

the contrast and more rapid the development. With a dilution of 1 part stock solution to 5 parts water, development time is 5-7 minutes.

(3) For tank development, including daylight developing tanks take one part stock solution to 10-15 parts water. Development time 10-15 minutes.

(4) For chloride (contact) papers dilute one volume with two volumes water. Development time 45-60 seconds.

(5) For bromide and chloro-bromide prints and enlargements. One part stock solution to 5-7 parts water. Development time  $1\frac{1}{2}$ -2 minutes.

### HIGH CONTRAST DEVELOPERS

While the formulae already given for contrast developers may be contrasty enough for general purpose there are cases where still higher contrast is wanted. High-contrast developers are needed not only for special purposes, such as process work, but in many cases for general commercial work as well, particularly in industrial and press photography. They also find wide applications for the development of X-ray and aerial film.

There is, however, a basic difference between these two main applications for contrast developers. While for process work the highest possible contrast is usually required, commercial and industrial work calls for developers which still give a good reproduction of half tones.

In this latter case, developers based on a high concentration of sodium carbonate are contrasty enough. The general concentration of the developer should also be high and the hydroquinone content should exceed the metol to quite a considerable extent (see Formulae 11-16, Table XX).

Where maximum contrast is required, the formula has to be based on the use of sodium hydroxide (see Formulae 21-29). The use of this alkali certainly leads to the desired result but offers a number of other inconveniences. Developers containing caustic alkalies have limited keeping properties and one will therefore, in many cases, prefer to make the developer up in two stock solutions of good keeping properties (see Formulae 30-34).

Hydroxides are not pleasant to handle, owing to their caustic properties, so formulae have been devised using

**XXII.—SPECIAL DEVELOPERS**  
*High Contrast (X-Ray, Aerial Film)*

	21 ID19	22 ID19R	23 D19	24 D19R	25 AN 30	26 G209a	27 AG 30	28 D82	29 D178
Metol	2.2	4	2	4.5	3.5	4	3.5	14*	—
Sodium sul- phite anhyd.	72	72	90	90	60	65	60	52.5	90
Hydro- quinone	8.8	16	8	17.5	9	10	9	14	45
Sodium carbon- ate anhyd.	48	48	45	45	34	44	40	—	—
Potassium bromide	4	—	5	—	2	5	3.5	8.8	30
Sodium hydroxide	—	7.5	—	7.5	—	—	—	8.8	18
Water to	1000	1000	1000	1000	1000	1000	1000	1000	1000
Dilution	—	—	—	—	—	—	—	—	2 : 1
Development Time (min.)	5	—	5	—	6-8	5-8	4-8	5	3-4

\* Add 48 ml. alcohol to the Limitial water volume.

**XXIII.—SPECIAL DEVELOPERS**  
*High Contrast (Two Solutions)*

	30 D 153	31 ID 13	32 AN 70	33 G 220	34 AG 70a
<i>Solution A</i>					
Hydroquinone	25	25	25	25	10
Potassium metabisulphite	25	25	25	25	10
Potassium bromide	25	25	25	25	2
Water to	1000	1000	1000	1000	1000
<i>Solution B</i>					
Potassium hydroxide	50	50	50	—	20
Sodium hydroxide	—	—	or 36	45	—
Water to	1000	1000	1000	1000	1000
<i>Working Solution</i> Equal parts A and B, 3-5 min.					



**XXIV.—SPECIAL DEVELOPERS**  
*Extreme Contrast (for Process Materials)*

	35 AN79b	36 D85 AN79	37 DP7d
	<i>Solution 1</i>	<i>Single Solution</i>	
Sodium sulphite anhyd.	1	30	60
Paraformaldehyde	30	7.5	15
Potassium metabisulphite	10.5	2.6	5
Water to	1000	—	—
	<i>Solution 2</i>		
Sodium sulphite anhyd.	120	—	—
Boric acid cryst.	30	7.5	15
Hydroquinone	90	22.5	45
Potassium bromide	6	1.6	3
Water to	3000	1000	1000
Dilution	1 part sol. 1 3 parts sol. 2	—	1:1
Development Time (min.)	2	2	2

paraformaldehyde which, as we already know (page 87), forms hydroxide with sulphites or bisulphites in solution. Several such formulae are given in Table XXIV. Again it is possible to make these up in two solutions for better keeping properties. The developing agent used for these high contrast developers is hydroquinone.

The addition of formaldehyde causes caustic alkali to be generated in the developer and formalin bi-sulphite compounds are formed. These keep the sulphite concentration at a low and constant level. The keeping qualities of the developer are not seriously affected, but the hydroquinone is more easily oxidised to quinone and semi-quinone. The latter acts as an accelerator causing rapid development of the silver halide grains and also a reduction of grains adjacent to

those already developed. This process of "infectious" development gives gradation curves with very high gamma and short toe as required for lith materials.

#### LOW CONTRAST DEVELOPERS

It was mentioned on page 66 that optimum exposure of a negative required that the shadows be recorded on the toe region of the characteristic curve. Average scenes, i.e. those with a subject brightness range of about 160:1 (log scale 2.2), can be accommodated on normal negative materials as shown in the characteristic curve on page 193. Also it can be seen that these materials can accommodate at best a scene with a brightness range of approximately 1000:1. However for certain special purposes such as photographing an eclipse of the sun, a lamp filament when lit etc., it may be necessary to record scenes with brightness ranges that may be as high as 1,000,000:1.

If the scene has a higher brightness range than 1000:1 considerable highlight detail would be lost as the highlights would be recorded on or beyond the shoulder of the curve where the density of the negative is approximately constant. It is possible to record subjects of extended brightness ranges by developing to a lower contrast value than normal. This could be achieved by diluting a conventional developer and or developing for a shorter time but this procedure would result in loss of emulsion speed and exposure latitude. With specially formulated low contrast developers (Table XXV) it is possible to record subjects of extended brightness range without loss of emulsion speed in the toe region and, because the characteristic curve is very flat (gamma 0.12-0.25), a tremendous increase in exposure latitude results.

The formulae of Table XXV contain a low concentration of developing agents and moderate concentration of sulphite as the main ingredients. Agitation must be efficient and uniform with these developers because density differences are small.

The contrast obtained with these developers varies with the nature of the emulsion used. As a general rule, thick emulsions afford a lower contrast than thin emulsions. The photographer must, therefore, alter the developing time to suit the subject brightness range and the negative material being used.



**CORRECT DEVELOPMENT—PERFECT GRADATION.**

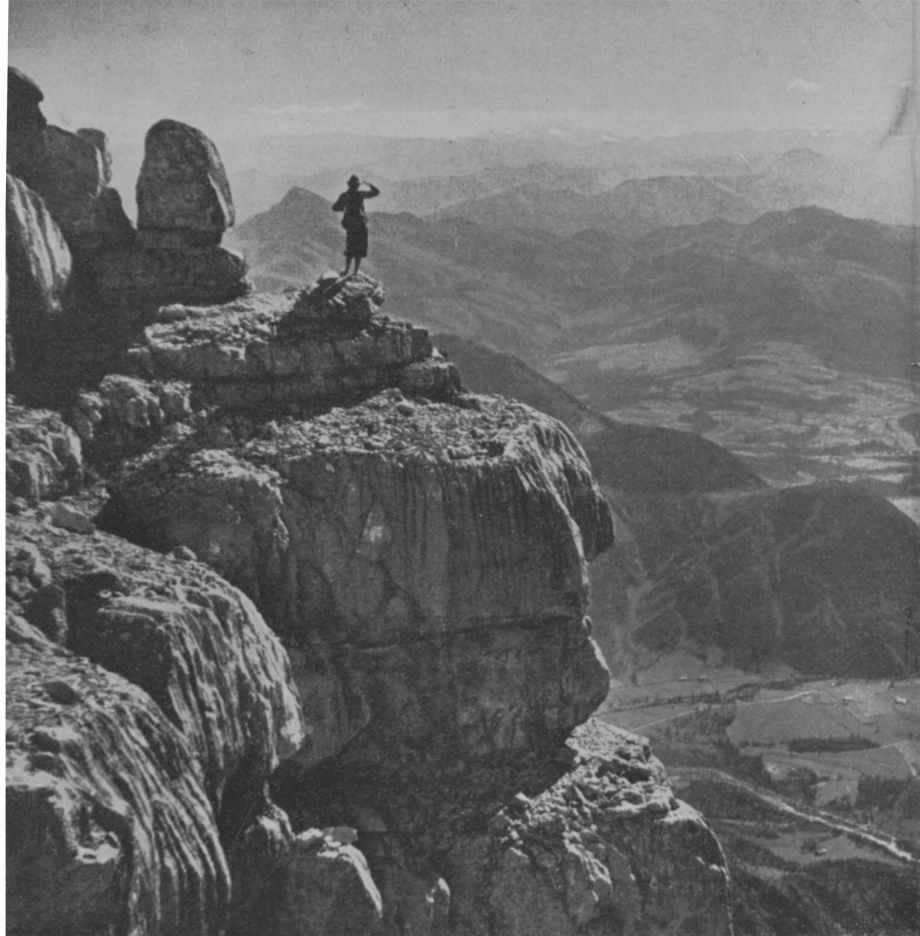
The obtaining of a picture that, from the deepest shadows right through to the highlights, reproduces a correct and natural scale of contrast is in the first case a question of the right choice of sensitive material (see page 30). The correct choice of negative material can, however, be completely nullified by inappropriate development and in this connection the formula used and the method of development can exercise a tremendous influence on the result. Only when negative material and development are perfectly suited to one another can a correctly-developed picture with perfect contrast, such as is shown in our illustration, be produced.—*Hugo van Wadenoyen.*



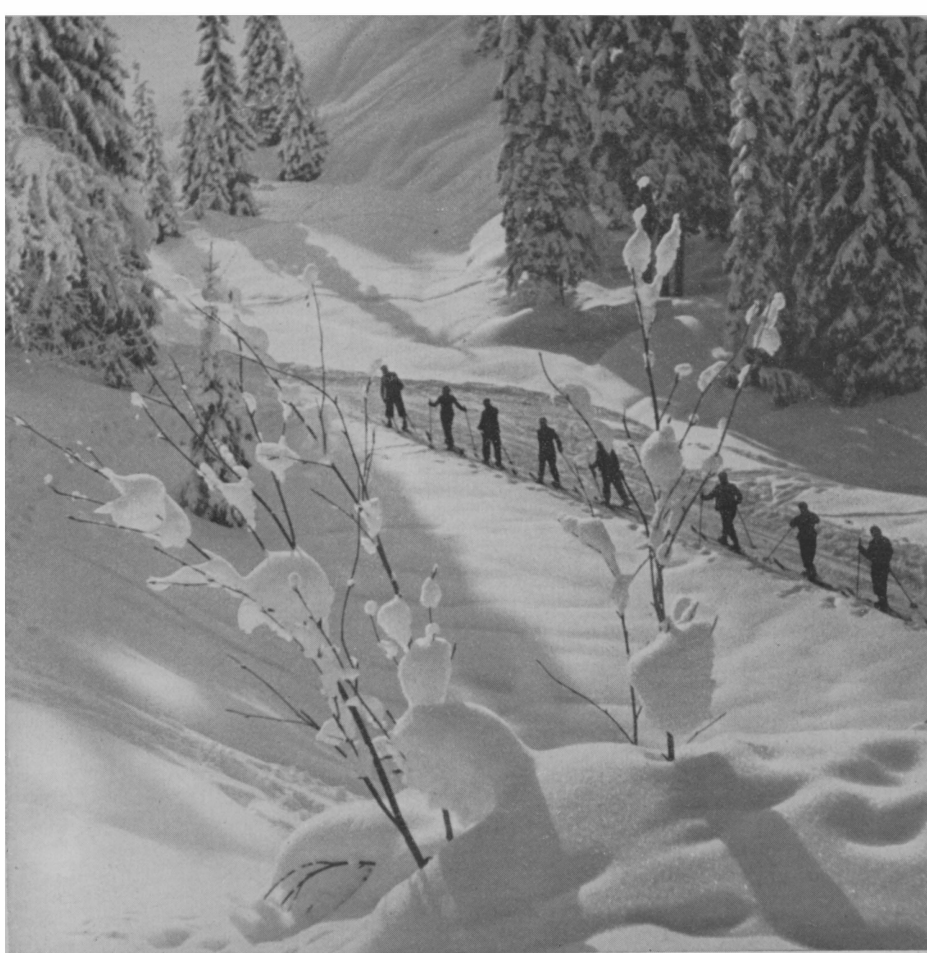


**DIFFERENT PICTURES—SAME DEVELOPMENT PROBLEM.** The appeal of the picture on the *left* lies in the brilliant lighting and the contrast between light and shade, whereas, in the picture *above* it is the delicate tone values which provide the attraction and reproduce the atmosphere of a rainy morning in early spring. In both cases the production of too hard a negative had to be avoided.

In the picture *opposite*, taken against the light, a contrasty developer would have produced deep shadows devoid of detail and chalky highlights. A soft-working compensating fine-grain developer (see page 210) is the correct formula to use in such a case. Such a developer is also suitable for the picture above so long as the negative material permits it and the necessary adjustment in exposure has been made. Otherwise a somewhat more energetic but still soft-working developer such as M-Q (see page 206) should be used or a diluted para-aminophenol (see page 197) developer.—*B. Pratchett and G. Schuh.*

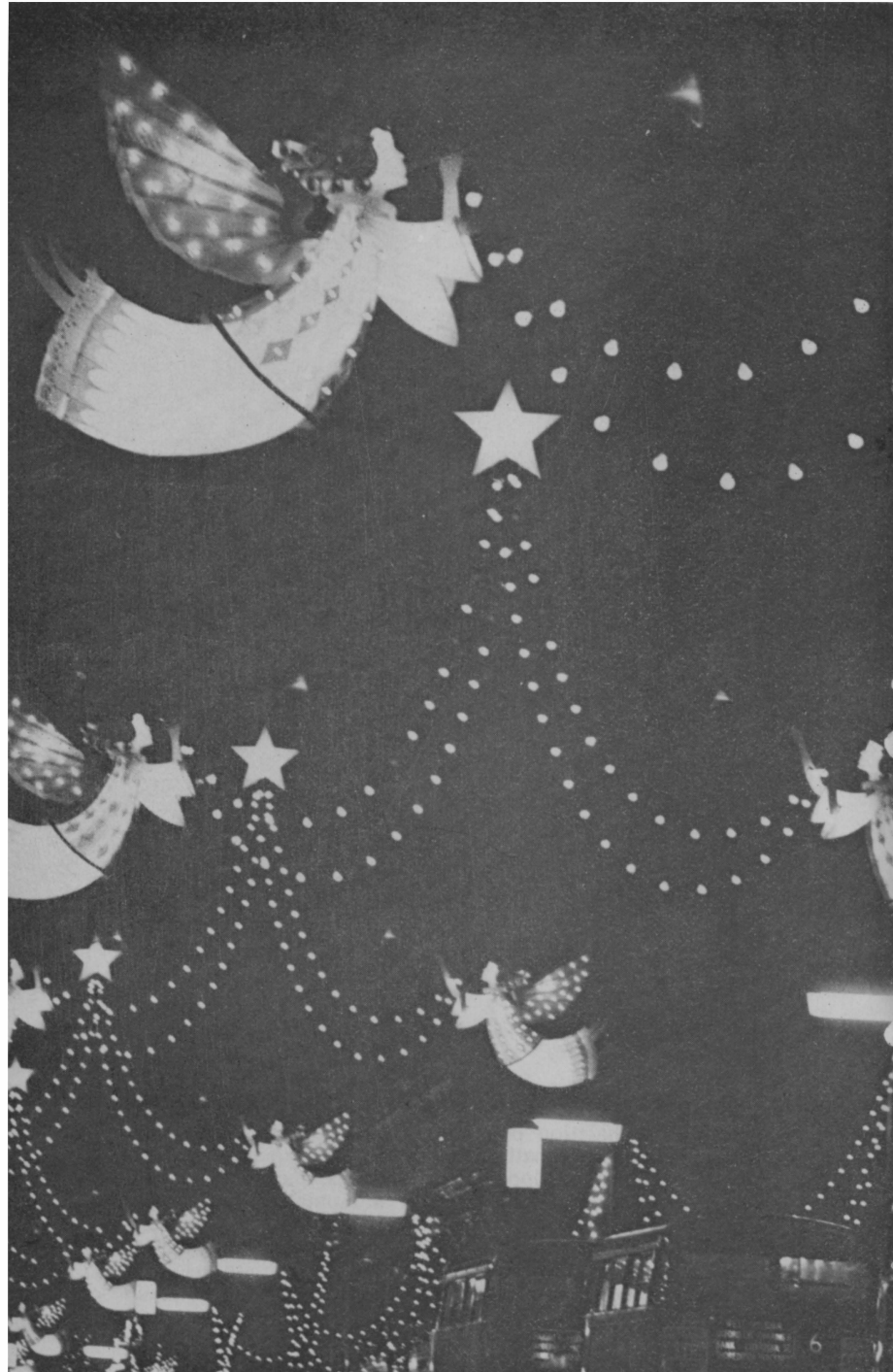


**AVOIDING EXCESSIVE CONTRAST.** This has been achieved in the pictures *above and opposite* by the use of an appropriate developer. A brilliant-working developer (page 174) would here have been a mistake, for it would probably have resulted in loss of detail in the distance and in the snow appearing like marble instead of appearing translucent. Developers which obviate both these possibilities are fine grain or high definition developers (see pages 202 and 214).

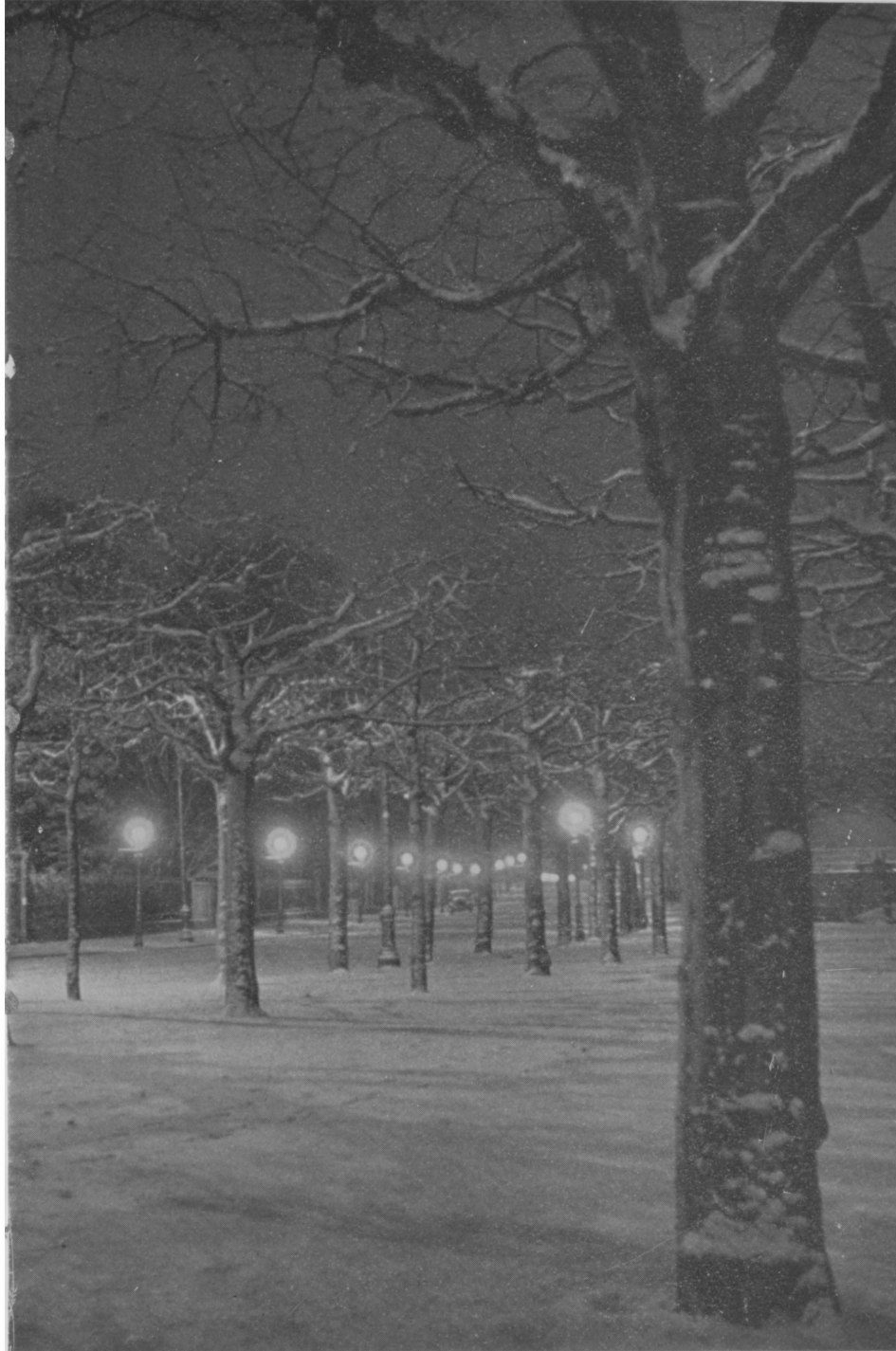


**AVOIDING HALATION.** As explained on page 69, the avoidance of halation is not merely a question of sensitive material, but also a matter of correct development. One must choose a surface developer, for example a fine-grain compensating developer (see page 203) or a tanning developer (see page 222). In the picture on page 186 halation is hardly perceptible, but in that on page 187 very characteristic and marked halation is seen in the street lamps. In neither of these cases was the development exactly right, but in neither case is the result unnatural.—*P. C. Poynter and P. Damm.*











**THE DEVELOPMENT OF PORTRAITS.** Portrait negatives require very special care in development if the fine shadows and details in the flesh tones are not to be lost. Moreover, that possibility is often increased by the photographer choosing somewhat strong lighting in order to obtain increased effect (*opposite*). Hence in developing portrait negatives the whole endeavour must be directed towards obviating contrast and obtaining modelling and detail as well in the deepest shadows as in the highlights. Many professionals hold the view that this can only be obtained by the use of a Pyro developer (see page 196), while others favour a diluted para-aminophenol (see page 197). Fine-grain developers are obviously applicable, but choice should be made of a formula which is not too soft-working, such as the borax M-Q developers (see page 206).—*Ralph Ballon and Leslie Turtle*

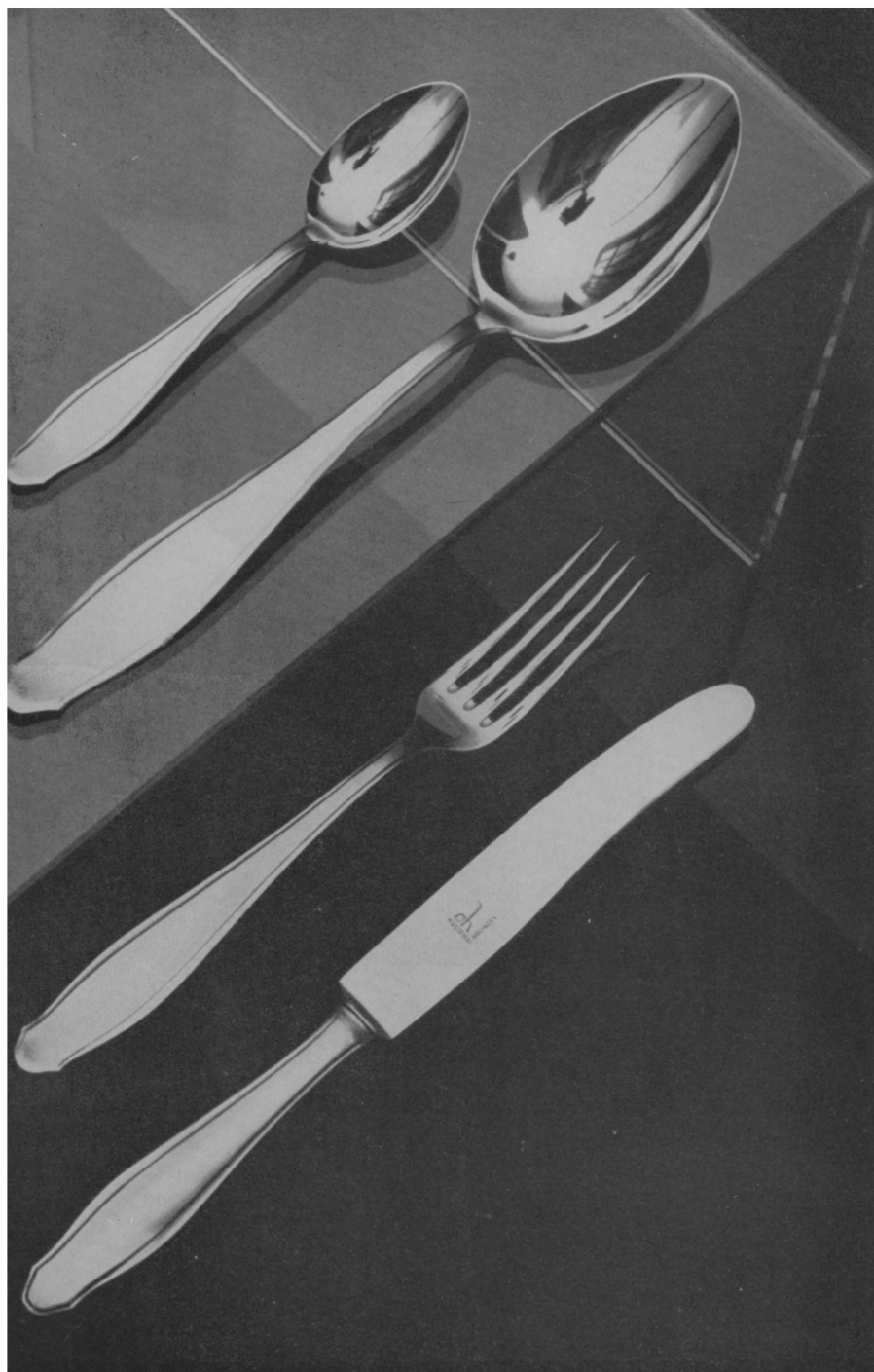




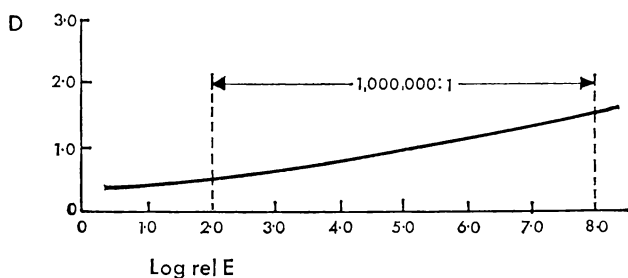
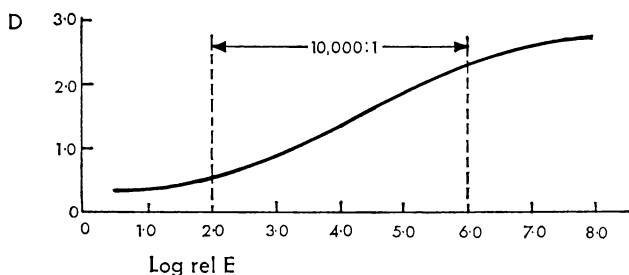
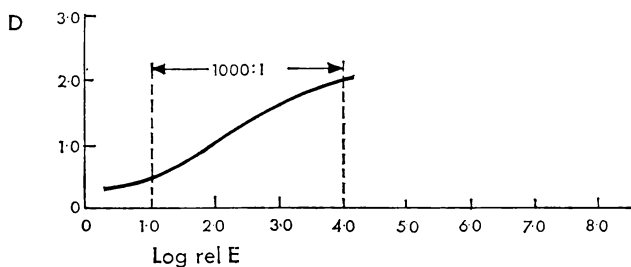
**AGAINST THE LIGHT.** The development of examples such as that *above*, where very strong light effects are present, is the same as for night photographs (page 185). In such a case as that *above* a tanning developer (page 222) is particularly suitable. Silhouettes (*opposite*) call for a pronouncedly contrasty or hard-working developer such as an M-Q contrasty developer (page 174).—J. Dulovits and Hugo van Wadenoyen.



COMMERCIAL PHOTOGRAPHS. With pictures as that on the *next page* it is essential that the subject be shown in good contrast with every detail clear and unmistakable and that the nature of the material composing the articles should be revealed. For this a brilliant working developer must be chosen such as the Focal Universal M-Q 16 (page 174), used at a dilution of 1:3 to 1:5.—*H. Gorny.*



## CHARACTERISTIC CURVES AND LOW CONTRAST DEVELOPMENT



**Top:** Normal development (D76 undiluted, 9 min.). The negative can only accommodate a subject brightness range of 1000:1.

**Centre:** Development in D76 diluted 1:1, 5 min. The negative can record a subject brightness range of approximately 10,000:1.

**Bottom:** Low contrast development (POTA, formula 39). The negative is able to accommodate a subject brightness range of 1,000,000:1 or greater.

**XXV.—SPECIAL DEVELOPERS**  
*Low Contrast (for Recording Scenes of Extended Brightness Range)*

	38 T/O XDR-4*	39 POTA**
Potassium sulphite	25	—
Sodium sulphite	—	30
Phenidone	—	1.5
Metol	1	—
Hydroquinone	1	—
Potassium bicarbonate	10	—
Water to	1000	1000
Development Time (min.)	4	2-7

\* Phot. Sci. Eng., 14, 363 (1967)

\*\* Phot. Sci. Eng., 11, 46 (1967).

#### OTHER DEVELOPING AGENTS

Metol and hydroquinone are the developing agents most frequently used but there are others that can be used for special purposes. Some well-known formulae and their important characteristics are listed in this section.

#### *Pyrocatechin*

*Important characteristics:* similar properties to hydroquinone. Special applications see page 222.

#### 40.—SINGLE-SOLUTION PYROCATECHIN DEVELOPER

Pyrocatechin	$\frac{1}{4}$ ounce	20 grams
Sodium sulphite, anhyd.	2 ounces	50 grams
Caustic soda	320 grains	16 grams
Potassium bromide	40 grains	2 grams
Water to make	16 ounces	400 ml.

To use, dilute 1 part with 10-15 parts of water. Development time 5 minutes.

*Caution:* The pyrocatechin must be dissolved only when all the other constituents are in complete solution. Does not keep well; should be made up immediately before use.



#### 41.—TWO-SOLUTION PYROCATECHIN DEVELOPER

A. Pyrocatechin	200 grains	10 grams
Sodium sulphite, anhyd.	$\frac{3}{4}$ ounce	20 grams
Water to make	20 ounces	500 grams
B. Potassium carbonate	2½ ounces	60 grams
Water to make	20 ounces	500 ml.

*Caution:* Dissolve the pyrocatechin after the sulphite.

For use take equal volumes of A and B. Time 7 minutes.

#### *Chlorquinol*

*Important characteristics:* Similar in properties to hydroquinone but more rapid working.

#### XXVI.—CHLORQUINOL DEVELOPERS

	42	43	44
	<i>Solution 1</i>	<i>Single Solution</i>	
Metol	—	—	8
Chlorquinol	25	50	50
Sodium sulphite anhyd.	100	100	100
Water to	1500	—	—
	<i>Solution 2</i>		
Potassium carbonate	—	300	250
Sodium carbonate anhyd.	120	—	—
Potassium bromide	2.5	5	2
Water to	1000	1000	1000
Dilution	3 parts sol. 1 2 parts sol. 2	1:3-5	1:5 1:10
Development Time (min.)	5-7	5-7	2-3 5

*Caution* In the metol-chlorquinol developer (Formula 44) both the metol and the chlorquinol must be completely dissolved before adding the sulphite.

## *Pyrogallol*

*Important characteristics:* gives negatives with delicate gradation and good detail. Owing to the ease with which pyro is oxidised in alkaline solution, single-solution developers are impracticable as they do not keep.

### 45.—TWO-SOLUTION PYRO DEVELOPER

A. Pyrogallol	2 ounces	50 grams
Potassium metabisulphite	88 grains	5 grams
Sodium sulphite, anhyd.	5 ounces	125 grams
Water to make	40 ounces	1000 ml.
B. Sodium carbonate, anhyd.	3 ounces	75 grams
Water to make	40 ounces	1000 ml.

For use take 1 part A, 1 part B and 4 parts water. Development time 6-7 minutes.

## *Glycin*

*Important characteristic:* Slow and clean working, giving low contrast and has good keeping properties.

### XXVII.—GLYCIN DEVELOPERS

	46 AN72	47 ID60	48 AG8	49 G204
Sodium sulphite anhyd.	125	20	12.5	15
Potassium carbonate anhyd.	250	60	25	60
Glycin	50	30	2	10
Methyl alcohol	—	—	—	10
Water to	1000	1000	1000	1000
Dilution	1:4 1:15	1:7	—	— 1:3½
Development Time (min.)	5-10 20-25	12-15	10-12	9 30

## *p-Aminophenol hydrochloride*

*Important characteristics:* rapid fog-free developer, not much affected by variations of temperature. Permits preparation of concentrated stock solutions.

## XXVIII.—P-AMINOPHENOL DEVELOPERS

	50	51	52
	<i>Solution 1</i>	<i>Single Solution</i>	
p-Aminophenol hydrochloride	25	100	7.3
Potassium metabisulphite	—	300	—
Water to	1000	—	—
<i>Solution 2</i>			
Sodium sulphite anhyd.	75	—	50
Potassium carbonate	150	—	—
Sodium carbonate anhyd.	—	—	50
Water to	2000	1000	1000
Sodium hydroxide (50% solution)*	—	qs**	—
Dilution	1 part sol. 1 2 parts sol. 2	1:20-25	—
Development Time (min.)	5-6	4-5	8-15

\**Caution* When making up 50 per cent sodium hydroxide heat is generated and the solution must be cooled before adding to the developer.

\*\*Add the 50 per cent sodium hydroxide solution dropwise until the precipitate which forms just redissolves.

More contrasty results can be obtained with Formula 51 by diluting the developer with only 10 parts of water.

## 53.—P-AMINOPHENOL-HYDROQUINONE DEVELOPER

	<i>Working Solution</i>	<i>Replenisher</i>
Kodolox (p-aminophenol oxalate)	1.5	8
Hydroquinone	2	3
Sodium sulphite anhyd.	50	50
Sodium hydroxide	3	7
Potassium bromide	2.5	—
Water to	1000	1000

*Caution:* Dissolve the sodium hydroxide separately in a small quantity of water, then add to the solution containing the other constituents already dissolved.

Development time 12-15 minutes.

*Important characteristics:* this developer has similar properties to a metol-hydroquinone tank developer, it does not keep quite so well and is perhaps not so energetic but its particular value lies in its usefulness in all cases where protection against metol poisoning is essential, although Phenidone-hydroquinone developer may serve equally well (see page 199).

### *Amidol*

*Important characteristic:* provides a rapid alkali-free developer.

#### 54.—AMIDOL STOCK SOLUTION

Sodium sulphite anhyd.	1 ounce	25 grams
Water to make	40 ounces	1000 ml.
To 4 ounces of this solution (100 ml.) 10 grains (0.5 gram) of amidol is added just before use.		

Development time 3-5 minutes.

*Caution:* The developer does not keep and should be discarded after use.

### *Phenidone*

*Important characteristics:* in combination with hydroquinone similar to M.Q. developers.

Phenidone has replaced metol in many formulae for general use as well as special purposes. It produces with hydroquinone a superadditive mixture in the same way as metol but is much more efficient in this respect. A given weight of hydroquinone requires about one quarter of its weight of metol to form an active mixture but only one fortieth part of its weight of Phenidone. This makes possible the formulation of highly concentrated developers with no tendency for the developing agents to crystallise out. The working solution of a P.Q. developer is, at the same pH, only slightly more active than a similar M.Q. developer. An increased quantity of Phenidone, however, produces the highly active type of developer required, for instance, for monobaths (see page 278).

Phenidone-based developers keep better than those based on metol. The reason is, as we have already seen in the paragraph on superadditivity (page 101), that the oxidation product of Phenidone is regenerated by hydroquinone in a much more efficient way than the regeneration of metol by hydroquinone. Furthermore, while the first oxidation

product of hydroquinone, namely its monosulphonate, forms an almost inert system with metol, it has with Phenidone a superadditive effect increasing developing power. It is thus obvious that Phenidone forms with hydroquinone very efficient developers of good keeping and exhaustion properties which are also easy to replenish. A number of such formula are recorded in Table XXIX. There are general purpose developers containing sodium carbonate as alkali.

**XXIX.—PHENIDONE-HYDROQUINONE (P.Q.) DEVELOPERS**

	General Purpose		Fine-Grain		High-Contrast		Concentrated Tank Sol.	
	55	56	57	58	59	60	61	62
	ID62	ID67	ID68	ID68 R	ID72	ID72 R	Nor-mal*	Con-trast*
Sodium sulphite anhyd.	50	75	85	85	72	72	125	120
Hydroquinone	12	8	5	8	8.8	12.5	16	20
Sodium carbonate anhyd.	60	37.5	—	—	48	48**	60	100
Borax	—	—	7	10	—	—	—	—
Boric acid	—	—	2	—	—	—	—	—
Phenidone	0.5	0.25	0.13	0.22	0.22	0.25	1	1.5
Potassium bromide	2	2	1	—	4	—	9	15
Benzotriazole 1%	20	15	—	—	10	8	300	—
Water to	1000	1000	1000	1000	1000	1000	1000	1000
Dilution	1 : 3 1 : 7	1 : 2 1 : 5	none	—	none	—	1 : 20 1 : 50	1 : 9
Development Time (min.)	3-4 6-7	4½ 9	8	—	5	—	11 15	3

\* A. Wiedermann, Sc.et.Ind.Phot., Vol. 32, 97-128.

\*\* and sodium hydroxide 7.5

Phenidone formulae require a rather high restrainer content; benzotriazole has to be used in addition to potassium bromide. With borax, fine grain developers can be prepared similar to their M.Q. counterparts. Highly concentrated P.Q. developers can be prepared by formula number 61, giving efficient developers even at a concentration of one part in 50 parts of water.

When making up these developers the constituents must be dissolved in the order given, as Phenidone is not soluble in water.

#### TANK DEVELOPERS

Tank developers intended to handle large numbers of plates or films must satisfy quite a number of conditions. As development is by time and a variety of films are developed together, the developer must possess such properties that its results are neither too hard nor too soft. The ratio of metol to hydroquinone, the quantity of these developing agents and that of the alkali must therefore be carefully adjusted to achieve the best compromise.

As tank developers are in use for weeks or even months they must have good keeping properties and not be easily exhausted. The sodium sulphite content should therefore be on the high side and the exhaustion taken care of by regular addition of a replenisher solution (see "R" in Table XXIX). During use the developer loses strength by chemical reaction and at the same time the level of the solution drops. Every film which passes through the tank removes a small quantity of solution and this loss must be made good by the addition of a solution of a composition very similar to that of the original developer. This is the strengthener or replenisher and it is added at suitable intervals and its concentration is so adjusted that it maintains the level of the liquid in the tank and at the same time the energy of the developer. As can be seen from Table XXX the composition of the replenisher is very similar to that of the original developer but it is usually a little more concentrated. It does not usually contain potassium bromide.

As mentioned above and on pages 74-76, developers require replenishment because their activities change during use. These changes in development activity may be summarised as follows:

- (1) The developing agent is used up by aerial oxidation and by oxidation during the development process (reduction of the silver halide to silver involves oxidation of the developing agent). The former causes the pH of the developer to rise and the latter causes the pH to drop. Thus the development

**XXX.—SPECIAL M.Q. DEVELOPERS**  
*Tank*

	63 DK 50	64 DK 50R	65 ID6	66 ID 6R	67 AN 47	68 AN 47R	69 Focal	70 Focal R	71 G 210	72 G 210R	73 AG 45	74 AG 46	75 AG 61	76 AN 48m	77 AN 48mR	78 ID 34	79 ID 34R
Metol	2.5	5	0.6	1.5	1.5	3	1	2	0.6	1.2	1	1.1	3.5	2	6.3	0.6	3.1
Sodium sulphite anhyd.	30	30	9	25	45	45	18	32	19	8	13	21.5	50	40	30	10	19.5
Hydroquinone	2.5	10	3.5	3	3	6	2	4	1.6	3.4	1.8	1.6	6.5	1.5	10	3.1	3.1
Sodium carbonate anhyd.	—	—	20	55	5	10	6	12	4	9	4.5	6	40	—	—	9	18
Kodalk	10	40	—	—	—	—	—	—	—	—	—	—	—	10	40	—	—
Potassium bromide	0.5	—	2.5	—	0.8	—	2	—	0.5	—	0.6	0.4	1	0.5	—	0.3	—
Sodium metabisulphite	—	—	10	25	1	2	—	—	—	—	—	—	—	—	—	2.5	—
Water to	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Development time (min.)	8		10		6-8		12		8		10-12	8-10	6-7	5-7		10	

activity is altered both by diminution of the concentration of the developing agent and by changes in pH although this effect is reduced by the inclusion of buffers in developer formulations (page 89).

- (2) Loss in developer due to carry over of the solution by the film.
- (3) The sulphite is used up by reaction with oxidised developing agent (page 81), which may result in stain and also affect the grain size (page 194).
- (4) The bromide content of the developer increases because bromide ions are released in the development reaction. This results in a slowing down of the development reaction (page 91).

In order to overcome these effects, which generally result in a decrease in developer activity, the developer must be replenished. The control of developer activity for the large scale user is given in the chapter on Quality Control.

#### FINE GRAIN DEVELOPERS

Fine grain development has played an important part in the history of modern negative technique. There was a time when it was considered as absolutely essential to reduce the size of the silver grain by fine grain development and numerous formulae were published to get this result. However, the importance of fine grain development has receded since. The main reason is that the granularity of the emulsion has itself been made so much finer that it is no longer so important to rely on the development process.

This does not mean that fine grain developers are completely obsolete. They are still essential for the production of a good negative—but in a different context. Modern emulsions still need fine grain development in the sense that a developer must be chosen which is suitable for these fine grain emulsions, in the following respect:

- (1) The developer must give the correct gamma and have no tendency to produce excessive contrast.
- (2) The developer must preserve the original fine grain of the emulsion and have no tendency to cause “clumping” of the grain.
- (3) If, in addition, the developer even reduces the



granularity, it is certainly a useful feature as long as it can be achieved without other important factors suffering.

We can thus define the fine grain developer as a developer which gives a low contrast without any, or at least any serious, loss of speed and without "clumping" of the grains. The developer may or may not actually improve the definition. We have therefore to deal with three types of developers specially suitable for fine grain materials:

- (1) Medium fine grain developers of the "retarded development" type (Table XXXI).
- (2) True fine grain developers, also called super or ultra fine grain developers (Table XXXII).
- (3) High definition developers (Table XXXIV).

All these developers act as "compensating" developers, i.e. they prevent the formation of heavy, unprintable deposits in highlight areas.

#### PRINCIPLES OF FINE GRAIN DEVELOPMENT

The question as to which factors have the main influence in fine grain development has attracted considerable research. From the many theories, the following two conclusions are generally admitted to be well founded.

- (1) The first condition which a fine grain developer must fulfil is that it shall be capable of dissolving the silver halide of the emulsion.
- (2) The second condition is that its energy of development shall be low so that its slow working will give a negative of medium contrast and density.

These two characteristics are found as we shall see in all fine grain developers and we are therefore dealing with them in greater detail.

A. *Solvent for a silver bromide.* If in any developer the sodium sulphite content is raised to about 100 grams of the anhydrous salt in one litre of water, the developer has solvent properties for silver halide. To enhance this further other solvents for silver halide have been suggested such as ammonium chloride, hypo, or thiocyanate. Their true value

is however doubtful as they tend to cause fog and have the tendency to reduce the speed of the emulsion.

The favourable action of p-phenylenediamine, the classical fine grain developer, can be explained too as being due to the fact that it is not only acting as a developer substance, but also as a solvent for silver halide. This developing agent has unfortunately a number of very unpleasant properties: it is poisonous, has very strong dyeing properties, and stains fingers and photographic utensils.

Hence it is important to have a developer which has the good without the bad properties of p-phenylenediamine. This has been achieved by combining p-phenylenediamine with other developing agents forming new compounds which have less objectionable properties (page 100). p-Phenylenediamine has also been successfully replaced by other organic solvents for silver halide which may not be useful developing agents themselves. A substance of this type is o-phenylenediamine, which is used in combination with metol. This developer gives excellent fine grain, has good keeping properties and shows no tendency to fog or stain (Formula number 98).

**B. Low developing energy.** When a film is fully developed the exposed grains are completely converted to metallic silver. When, however, the film receives only partial development to a lower contrast, most of the exposed grains are only partially developed and give therefore smaller particles of metallic silver (page 52). To obtain such an effect of retarded development the alkalinity of the developer has to be reduced. This can be done simply by having a very low alkali content in the formula. Some fine grain developers contain therefore sodium carbonate only at a fraction of the normal amount. An alternative method is to replace this alkali by weaker substances such as borax or Kodalk. This, of course leads to developers with lower pH and a glance at Table XXXI will show us which level we have to take. We might also use one of the buffer mixtures which help to maintain the pH value of the developer solution and to achieve consistent results.

#### MEDIUM FINE GRAIN DEVELOPERS

The more well-known metol-hydroquinone formulae of this type are summarised in Table XXXI. It will be seen that all

are characterised by high sulphite content and either low or weak alkali content. The sulphite content is around 100 grams per litre to give the developer good solvent properties for silver halide.

The column "Alkali" of this table reveals a number of interesting facts. In Formula 88 sodium carbonate is used at the comparatively low concentration of 5-6 grams per litre. In Formula 80 which represents Kodak D76, one of the most popular fine grain developers of this type, borax is added as an alkali. Wherever borax is used in any developer, the granular or crystallised quality should be used as these are more easily soluble than the powder form which has the tendency to float on the surface of the solution and is only very slowly dissolved. If, in Formula 80 or similar formulae, the borax is replaced by an equal weight of Kodalk, a somewhat more energetic developer is obtained allowing somewhat shorter developing times. At the same developing time a little higher contrast would be obtained while the grain size is not noticeably affected. All these developers lend themselves excellently to tank development but for large-scale use a replenisher solution is required, for reasons which are discussed on page 76. Replenishers for some of the fine grain developers are listed in Table XXXI under Reference "R".

As we already know, the use of an alkaline buffer mixture offers advantages as far as the exhaustion properties of the solution are concerned. Such a formula is No. 85. It must be noted that developers of this type are, in general, somewhat softer-working and give lower effective film speed than the standard D76 formula.

An interesting fact is that Formulae 82, 83 do not contain any added alkali. These developers rely on the alkalinity of the sodium sulphite itself which has a pH value of 8-9. In this way excellent but somewhat slow-working fine-grain developers can be obtained. There is no point in using hydroquinone in these developers: it would not contribute to the developing properties under these conditions.

Formulae of type 83 go a step further in this direction. The alkalinity of the sodium sulphite is still further reduced by the addition of sodium metabisulphite. These developers have the lowest activity of all developers in this group and give the finest grain and also the lowest contrast.

Going too far in this direction would be fatal: the speed

**XXXI.—SPECIAL M.Q. DEVELOPERS**  
*Fine Grain*

	80 D76	81 D76R	82 D23	83 D25	84 D25R	85 D76d	86 ID11	87 ID11R	88 AN12	89 AN17	90 AN17R	91 G206	92 G207	93 AG44
Metol	2	3	7.5	7.5	10	2	2	2	8	1.5	2.2	2	4	1.5
Sodium sulphite anhyd.	100	100	100	100	100	100	100	100	125	80	80	100	100	80
Hydroquinone	5	7.5	—	—	—	5	5	7.5	—	3	4.5	4	—	3
Sodium carbonate anhyd.	—	—	—	—	—	—	—	—	5.75	—	—	—	5.8	—
Borax	2	20	—	—	—	8	2	20	—	3	18	2	—	3
Kodalk*	2	20	—	—	20	—	—	—	—	—	—	—	—	—
Potassium bromide	—	—	—	—	—	—	—	—	2.5	0.5	—	—	2	0.5
Special additions	—	—	—	Sod. Meta- bisul- phite 15	—	Boric acid 8	—	—	—	—	—	—	—	—
Water to	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Development time (min.)	4-8		4-8	15-20			6-11		10-15	10-15		8-10	8-10	

\*Kodalk is no longer available. For every 10 g. of Kodalk add 1.3 g. of sodium hydroxide and 6 g. of borax.

of the film would suffer to a very considerable degree. All true fine grain developers reduce the speed of the emulsion to some degree compared with that obtainable by full development in a normal developer. However, in most cases the loss of speed is negligible and within the latitude of the emulsion. Nevertheless, when using fine-grain developers of the lowest activity such as Formula 83 it is advisable to give ample exposure.

Phenidone (page 101), has been used in combination with hydroquinone to make up "medium fine grain developers". Formulae for a developer like that together with the necessary replenishers have been published by A. J. Axford and J. D. Kendall. As shown in Formula 94 they recommend two types of replenisher, one for the topping-up method of replenishing, and another for the bleed system. The differences between these methods are as follows:—

In the topping-up method (page 159), the developing solution is maintained at a constant level by adding from time to time a certain quantity of the replenisher so that the loss of solution by developer carried over in the gelatine or on the surface of the material, is replaced. In the bleed system which is normally only used in large-scale processing, used developer is run off and replenisher fed in continuously so that the level of the developer and its photographic characteristics remain fairly constant. The bleed system has the advantage over the topping-up method that a very high degree of constancy can be maintained, provided of course that the replenishing is controlled properly.

#### 94.—PHENIDONE-HYDROQUINONE FINE GRAIN DEVELOPER

	Working Solution	Replenisher	
		Topping-up Method	Bleed System
Sodium sulphite anhyd.	100	100	100
Hydroquinone	5	8	6.25
Borax	3	9	4
Boric acid	3.5	1	2.5
Potassium bromide	1	—	—
Phenidone	0.2	0.24	0.22
Water to make	1000	1000	1000
pH	8.95	9.28	9.09
Developing time	10 minutes at 68°F. 20°C		

## EMULSION SPEED AND FINE GRAIN DEVELOPMENT

When comparing the graininess characteristics of developers it is important to consider the relative emulsion speeds. A proper comparison can only be carried out if the negatives are developed to the same gamma. In fine grain work this should be 0.6-0.7. Under these conditions the emulsion-speed ratio of the four classes of developers is as follows:

- (a) To achieve low contrast with a normal M.Q. developer (page 174), the negative has to be under developed, with a consequent loss of speed that might amount to 50%. If—on the other hand—we develop the negative completely out, without any regard to contrast, we would make full use of the maximum speed of the emulsion, but the negatives might show a very coarse grain.
- (b) With fine-grain developers (Table XXXI) we can obtain low contrast without noticeable loss of emulsion speed as compared with the manufacturer's speed figure and without interfering with the original fine-grain characteristics of the emulsion.
- (c) With super-fine grain developers (Table XXXII) the same result is obtained, possibly with improved granularity. Emulsion speed, however, is reduced to about 60-70% of that given by ordinary fine-grain developers.
- (d) High-definition developers (Table XXXIV) give good negative quality, i.e. correct low contrast without effect on the grain, and also improve definition. There may even be a gain of speed compared with ordinary fine-grain developer.

## SUPER-FINE GRAIN DEVELOPERS

The classical super-fine grain developer is p-phenylenediamine which is capable of giving an exceedingly fine grain, but requires strong over exposure and a very long developing time and even then the contrast of the negatives is rather low. In addition, as we already know, this developing substance has a number of rather unpleasant properties. This naturally led to research for other additions which would have the

effect of shortening the developing time, increasing contrast, and if possible avoid the disagreeable properties of para-phenylene diamine.

The first step in this direction was the Sease formula (Formula 95) which contains glycin. The mixture of the two developing agents gives a fine-grain developer with improved photographic properties as far as emulsion speed and rate of development is concerned, but the solution has still the unpleasant properties of p-phenylenediamine. The same considerations apply to Formula 104 which contains metol. An improvement in this respect is the developing agent Meritol, a compound of p-phenylenediamine with pyrocatechin (Formulae 96 and 97 of Table XXXII). However, Meritol is not now generally available and has been superseded by other developing agents some examples of which can be found in Table XXXII.

There are now available quite a number of derivatives of p-phenylenediamine (see page 370) as these have found wide application in colour developers. These substances are much superior in many ways to p-phenylenediamine itself but they are not capable of producing quite such a fine grain. Formulae of this type are Nos. 99-100. In Formula 95 use has again been made of the accelerating effect of glycin. In Formula 100 hydroquinone is used for the same purpose.

There have been efforts to replace p-phenylenediamine by other agents. A successful result is the Windisch formula (No. 98) which makes use of o-phenylenediamine. This agent has only weak developing properties but is a good solvent for silver halide. The developing agent in the formula is metol.

The attempt to find suitable fine grain developers in other chemical groups has not been very successful. An exception is the M & B formulae (Nos. 102-103) based on the use of hydroxethyl-o-aminophenol. It is interesting to note that glycin has an accelerating effect on this developing agent, too.

As far as the general composition of these super-fine grain developers is concerned, a glance at Table XXXII shows that nearly all of them make use of the effect of a high sodium sulphite content. As alkali they are using either small quantities of sodium carbonate or borax. There is also one formula containing the buffer mixture borax—boric acid (Formula 100), while, in the Windisch formula No. 98 the pH of the sodium sulphite is reduced by the addition of sodium meta-

**XXXII.—SPECIAL DEVELOPERS**  
*Super Fine-grain Formulae*

	95	96	97	98	99	100	101	102	103	104
	<i>Sease</i>	<i>Meritol</i>	<i>Meritol-Metol</i>	<i>Windisch</i>	<i>Focal</i>	<i>FX 10</i> ( <i>G. W. Crawley</i> )	<i>Kodak</i> <i>US Pat.</i> 2193015	<i>M. &amp; B.</i>	<i>M. &amp; B.</i>	<i>ppd-Metol</i>
Developing agent(s)	A 10 E6-12	G16	F2.3 G13.7	B12 F12	C20 E20	C6 J6	D5	H6	H6 E1.16	A5 F10
Sodium sulphite anhyd.	90	90	90	90	100	100	30	100	100	60
Sodium carbonate anhyd.	—	—	—	—	—	—	30	11.5	11.5	10
Borax	—	—	—	—	20	4	—	—	—	—
Potassium bromide	—	—	—	—	—	—	—	0.6	—	1
Other additions	—	—	—	Sod. meta bisulphite 10	—	Boric acid 4	—	—	—	—
Water to	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Development time (min.)	15	14-18	7-9	12-13	Dil.1:7 12-15	8	20	15-20	6-10	8

A. p-phenylenediamine

B. o-phenylenediamine

C. Diethyl-p-phenylenediamine bisulphite (Genochrome, Activol)

D. 4-amino-N-ethyl-N ( $\beta$ -3-methane sulphonamido ethyl) m-toluidine sulphate (CD3, Mydochrome)

E. Glycin

F. Metol

G. Meritol

H. Hydroxyethyl-o-aminophenol

J. Hydroquinone



**bisulphite to decrease the activity of the developer and to produce a finer grain.**

#### FILM SPEED AND EXTENDED DEVELOPMENT

Because of the availability of wide-aperture lenses and fast films, there are few occasions when a photographer cannot obtain a satisfactory exposure, even under very low levels of illumination. Nevertheless, there are times, such as when photographing floodlit sports events where high shutter speeds are required, when the film speed could be usefully increased. A technique of film development called "push-processing" enables a photographer to give less than ideal exposure but still obtain reasonable results.

As a general guide it is possible to underexpose a film by one stop and compensate by increasing the development time by 50%. This is equivalent to a doubling of the film speed, and a 400 ASA film would be rated at 800 ASA. Although it is possible, depending on the results required, to increase the film speed by more than one stop this seldom produces acceptable results. The only judge of whether results are acceptable must be the photographer. Obviously the subject matter will greatly influence this decision.

As with most things, you never gain something for nothing, and the quality losses for push-processing a film include:

- (1) *Loss of shadow detail.* This is caused by underexposure of the film. A film normally rated at 400 ASA but push-processed to 800 ASA does not have the true speed of a genuine 800 ASA film, and is unable to record as low a level of subject brightness. The genuine 800 ASA film will produce greater shadow detail than the 400 ASA film push-processed to 800 ASA. The greater the degree of underexposure the greater the loss of shadow detail. For some photographic assignments shadow detail may be important.
- (2) *Increase in contrast.* As film development is increased then so is the resultant negative contrast (see page 213). However, with a subject of normal brightness range it is usually possible to produce acceptable prints by using softer grades of paper, provided that the film is not push-processed to

extremes. A subject of lower than average brightness range can be successfully push-processed to a greater extent. Conversely, subjects of higher than average brightness range can not be push-processed to any great extent unless considerable loss of subject information is acceptable. For example, highlight information can be retained at the expense of shadow and mid-tone detail.

- (3) *Increase in graininess.* As with all films that are overdeveloped the graininess will increase. The greater the overdevelopment (push-processing), the greater the graininess. For some purposes, a print with increased graininess may be more pleasing than a "normal" print.

It must be emphasised that any increased development technique does not change the film speed, which remains largely unaltered, but gives a more useful camera exposure and a "printable" negative.

Obviously any practical applications of the push-processing technique must take into account the film/developer combination used and the camera equipment. Practical film speed ratings depend not only on the accuracy of the equipment (e.g. shutter speed, exposure meter) but also on how it is used. It is very advisable to run tests before any important assignment is undertaken.

Table XXXIII below gives a simple practical method for determining the effective film speed rating using your own equipment and your own judgement of image quality.

**XXXIII.—FILM SPEED RATING EXPOSURE TEST**

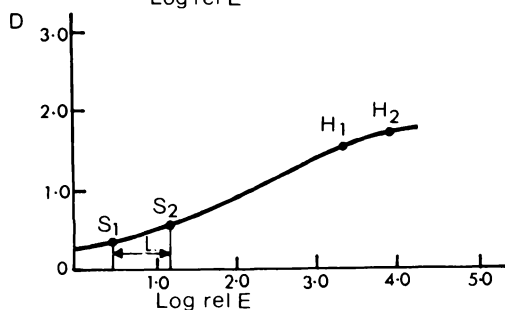
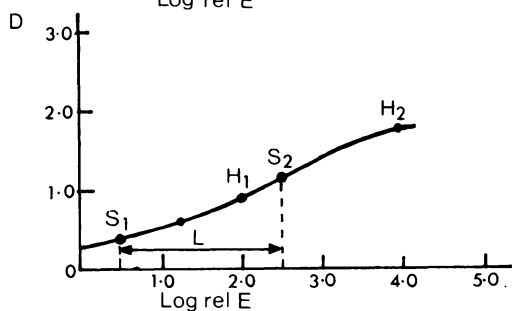
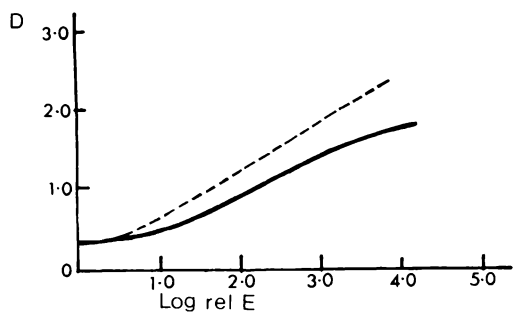
Camera exposure Change ( <i>f</i> stops)	—4	—3½	—3	—2½	—2	—1½	—1	—½	N	+½	+1
ASA factor (X)	16	11	8	5.6	4	2.8	2	1.4	1.0	0.7	0.5

N—corresponds to a "normal" exposure.

In order to determine the effective film speed rating the following procedure is recommended (Kodak pamphlet AJ-30):

Select a scene of average contrast and set your camera or exposure meter to the ASA speed of the film being used.

# CHARACTERISTIC CURVES, EXTENDED DEVELOPMENT AND EXPOSURE LATITUDE



*Top:* Increase in contrast for twice the normal development time is shown by the dashed curve when compared with the normal time (full curve).

*Centre:* Large exposure latitude ( $L$ ) for low contrast scenes.  $S_1$ ,  $H_1$  are shadows and highlights for minimum acceptable exposure, and  $S_2$ ,  $H_2$  are those for maximum acceptable exposure.

*Bottom:* Small exposure latitude for contrasty scenes.  $S_1$ ,  $H_1$  and  $S_2$ ,  $H_2$  are defined as above.

Determine the required exposure as carefully as possible. Using Table XXXIII make a series of exposures on the film at half stop changes from the indicated exposure. Identify each negative either by noting the frame number against the exposure given, or preferably by including in each exposure a clearly written card with the exposure information.

Repeat the same exposure series on a roll of the same film (same emulsion batch). Then process one roll of film in the developer for the recommended time and the other roll for a 50% increase in developing time. Use the same temperature and agitation technique for both films. Make prints from all reasonable negatives, using the appropriate grade of paper. Some of the negatives will be too "thin" to give acceptable results.

Examine the prints and select the best one from the normally processed roll. This should correspond to the negative exposed with an ASA factor of one (N). A substantially different factor to 1.0 means that your equipment should be checked. From the push-processed film select the print that appears acceptable to you at the highest ASA factor.

Table XXXIII gives the factors by which the stated ASA speed of the film must be multiplied to give the practical ASA speed rating. For example if a film of ASA speed 400 was used and an acceptable print obtained from the push-processed film at an exposure of two stops under ( $-2$ ) the practical ASA speed rating for your use would be 1600 ( $400 \times 4$ ).

Thus in practice films may be rated at higher speeds than their true ASA speed but real methods of increasing film sensitivity are discussed on pages 256–262. These latter methods are normally used only under controlled conditions by photographic specialists such as scientific photographers or astronomers who require images to be recorded under very adverse lighting conditions.

#### **HIGH-DEFINITION (HIGH ACUTANCE) DEVELOPERS**

This group has become one of the most important because the developers it includes lead to negatives of enhanced acutance and prints of good image sharpness (see page 58).

To make full use of the advantages of this type of developer it is, of course, advisable, as we have already seen on page 62, to choose a fine-grain, thin-emulsion film of low

or medium speed. It is doubtful whether, for these films, fine grain developers are the best to use. Modern films of this type are already so fine in grain that there is really no need for further improvement. Nevertheless, it is important to get the best possible result as far as negative quality and emulsion speed is concerned.

To get the optimum negative quality with these thin emulsion films the problem must therefore be approached in a quite different way. Let us consider the various properties a developer should have to give the best results with fine grain films. These films tend to yield excessive contrast and one of the properties of the developer should therefore be the reduction of contrast. However, while the contrast should be reduced the gradation must not suffer i.e. the tone scale must not get too restricted. We, therefore, need basically a soft-working developing agent such as metol. It should also be a compensating developer (see page 139) i.e. the concentration of the developer should be comparatively low so that it exhausts rapidly in the highlight areas. But a diluted developer may not develop shadow details adequately, which amounts to a loss of emulsion speed, so the alkali content should be relatively high.

Such a developer, having a low concentration of developing agent, the activity of which is maintained by high alkali content, has at the same time a tendency to produce the border effects which we have mentioned before (page 77). The diluted compensating developer becomes quickly exhausted over the dark areas where a lot of silver halide has to be developed. The exhausted developer meets active developer at the border of the dark area and the action of both naturally spreads somewhat in the neighbouring areas. The result is that the active developer of the light area carries over and continues to develop the edge of the dark area. On the other side the exhausted developer of the dark area migrates to the light area and retards development there. The result is that the "sharpness" of the outline is increased due to the higher edge-contrast (page 217).

Table XXXIV gives formulae for a number of such high-definition developers. They are all characterised by the fact that the concentration of developing agent is very low, approximately in the region of only .5 grams per 1 litre. However, the activity of the developers is maintained by a

# XXXIV.—SPECIAL DEVELOPERS

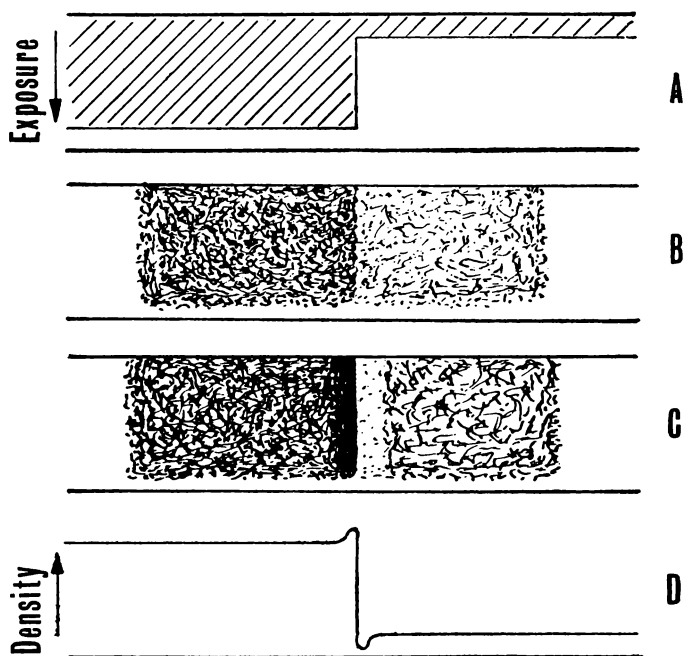
## High Definition

	105 W. Beutler	106 Windisch	107 FX1 G. W. Crawley (Brit. Journ.)	108 FX2 G. W. Crawley	109 FX13 G. W. Crawley
Metol	5	—	0.5	0.25	0.5
Glycin	—	—	—	0.75	—
Pyrocatechin	—	12.5	—	—	—
Sodium sulphite anhyd.	25	80	5	3.5	40
Sodium carbonate anhyd.	25	—	2.5	—	2.5
Potassium carbonate	—	—	—	7.5	—
Special additions	—	—	Pot. Iodide 0.001% 5 ml.	Ilford Desensitol Yellow Sol. 3.5 ml.	Pot. Iodide 0.001% 5 ml.
Water to	1000	1000	1000	1000	1000
Dilution	1 : 10	25 ml. + 15 ml. Pot. Hy- droxide 10% + 960 ml. water	—	—	—
Development Time (min.)	7-10	15-20	15	15	10

comparatively high alkali content. In Formula 106 the compensating effect has been increased by the choice of pyrocatechin as a developing agent which has a selective imagewise tanning effect on the gelatine of the emulsion (page 222).

These developers are also characterised by the absence of bromide which enhances local developer exhaustion at the boundary between high and low density areas. Agitation of these developers must be carefully controlled because too vigorous agitation neutralises the adjacency effect and too little causes streamers.

## ADJACENCY EFFECTS IN DEVELOPMENT



The active developer of light areas carries over and continues to develop the edge of the dark area while the exhausted developer of the dark area migrates to the light area and retards development there. The result is that the "sharpness" is increased due to the higher edge contrast. High definition developers are based on this effect.

All these high-definition developers can only be used once. It is, therefore, advisable to make them up either in the form of a concentrated stock solution or in the form of two solutions, of which one contains the developing agent and sulphite in 500 ml. of water, and the other the sodium carbonate in the remaining 500 ml.

#### INVERSION AGITATION

It has already been mentioned (page 78) how important it is to agitate the film in the tank properly, especially when spiral tanks are used for development. In these tanks the coils of the film are quite close together and unless the solution is kept on the move, the negatives may not be evenly developed. Rotating the spiral with a stirring rod is not a fool-proof method as agitation may not be quite even.

Inversion agitation eliminates the danger of uneven development. Many modern tanks are provided with a plastic cap which fits over the pouring opening of the tank lid. With the cap in position the tank is water-tight and can be turned upside down. Sufficient space is provided in the tank above the normal level of the solution so that when inverted a substantial portion of the solution flows across the film coils. To obtain the full benefit of this method, the tank must not be filled beyond the volume of solution prescribed by the manufacturer.

For inversion agitation the tank is turned upside down and held in this position until the developer has stopped running into the lid. Then the tank is turned back again. At the beginning of the development, repeat this half a dozen times or give the spiral a few twists with the stirring rod to dislodge any air bubbles. Then invert the tank for about 10 seconds (4 inversions) at 1 minute intervals throughout development.

#### PHYSICAL DEVELOPMENT

Physical developers, which differ from chemical developers in that they contain silver salts, were originally used almost exclusively for special purposes in scientific and technical photography. Later, they were found of particular interest in general photographic work, owing to their property of developing a fine grain. Today they are of academic interest only.



Formulae for physical fine grain developers specially devised for sensitive materials of that time were put forward by Odell and improved formulae were put forward by Turner.

The process consists of the following steps.

- (1) Treatment in a forebath.
- (2) Development in the silver-containing solution.
- (3) Fixing in an acid hardening-fixing bath.
- (4) Washing and drying.

Development can be carried out in a dish, but a tank is preferable. It is, of course, essential that the material of the vessel, whether dish or tank, should not be such as to precipitate the silver from the bath. Glass, porcelain, hard rubber or plastic can be used, but metals are not permissible, with the exception of certain types of stainless steel. Vessels and solutions used for the preparation of the developer and the development tank or dish must be scrupulously clean. Undissolved chemicals or dust particles etc. can act as nuclei for the precipitation of silver.

#### 110.—FOREBATH FOR PHYSICAL DEVELOPMENT

Potassium iodide	100 grains	5 grams
Sodium sulphite, anhyd.	$\frac{1}{2}$ ounce	12.5 grams
Water to make	20 ounces	500 ml.

The film is placed in the dish or tank dry and the forebath is then poured upon it and allowed to act for 3-4 minutes. The forebath is then poured off and can be used again and again, usually serving for at least eight treatments. The film is then rinsed well in two changes of water. Panchromatic films may be desensitised in the usual manner before being placed in the forebath (see page 252).

For development a concentrated silver-stock solution is prepared. It is of the utmost importance that the directions for making this solution be carefully and accurately followed.

#### 111.—PHYSICAL DEVELOPER

A. Silver nitrate	$\frac{1}{2}$ ounce	12.5 grams
Distilled water	8 ounces	200 ml.
B. Sodium sulphite anhyd.	2 ounces	50 grams
Distilled water	20 ounces	500 ml.
C. Hypo crystals	6 ounces	150 grams
Distilled water to	40 ounces	1000 ml.
D. Metol	40 grains	2 grams
Hydroquinone	80 grains	4 grams
Sodium sulphite anhyd.	$1\frac{3}{4}$ ounces	40 grams
Tribasic sodium phosphate	$1\frac{1}{2}$ ounces	32 grams
Distilled water to	40 ounces	1000 ml.

Solutions A and B are prepared warm (about 120°F., 50°C.) and allowed to cool to about 75°F. (24°C.). The solution A is poured slowly with constant stirring into solution B. Stirring must be continued until the white precipitate which forms initially is completely dissolved. When this is accomplished solution C is added to the mixture of solutions A and B to give the silver stock solution which has good keeping properties.

When the film has been treated in the forebath and received its two good rinsings it is placed in the physical developer solution consisting of 1 part of the silver stock solution (A + B + C), 1 part of the exciter solution (solution D) and 3 parts of distilled water.

#### **XXXV.—APPROXIMATE TIME OF PHYSICAL DEVELOPMENT**

<i>Film Speed</i>	<i>Development Time at 65°F.</i>
ASA 50-125	29 min.
„ 160-320	34 „
„ 400-800	36 „

When development is complete the film is given a good rinse and is then fixed in a normal acid hardening and fixing bath. (See page 273.)

As the silver bromide in the emulsion will have been partially converted into iodide in the forebath, a much longer fixing time will be necessary than that required for a normally developed negative, certainly not less than about 20 minutes: after that the film should be well washed and, before drying, the developed surface should be gently wiped over with a wad of cotton wool to remove any loose deposit of reduced silver.

Further formulae for physical development have been devised as a result of the careful investigations of F. R. McQuown. It is claimed that by this method the over-exposure usually called for is not necessary.

#### **112.—FOREBATH FOR PHYSICAL DEVELOPMENT (F. R. McQUOWN)**

Potassium iodide	120 grains	6 grams
Sodium sulphite, anhyd.	280 grains	14 grams
Borax powdered	50 grains	2.5 grams
Water to make	20 ounces	500 ml.

All the chemicals can be dissolved together. The borax

may be omitted if the bath is to be used up within a week or so. The bath can be used repeatedly. The film is immersed, without previous wetting, for 40 seconds in the forebath with vigorous agitation. After the forebath treatment rinse the film in water for 20 seconds and proceed to develop in the working physical developer solution.

### 113.—PHYSICAL DEVELOPER (F. R. McQUOWN)

Sodium sulphite, anhyd.	2 ounces	50 grams
Silver nitrate, cryst.	130 grains	6.5 grams
Borax, powdered	130 grains	6.5 grams
Hypo (Sodium thiosulphate)	2½ ounces	60 grams
Water to make	20 ounces	500 ml.

The sulphite should be dissolved in about 14 ounces (350 ml.) of water at about 120°F. (50°C.). The silver nitrate is dissolved in about 4 ounces (100 ml.) of water and slowly added to the sulphite solution which is vigorously stirred. The other chemicals are then dissolved in the order named and the volume made up to 20 ounces (500 ml.).

The plate or film is immersed in the following working solution:

Developer stock solution	1 ounce	25 ml.
Water to make	4 ounces	100 ml.
Amidol	6 grains	0.35 grams

The working solution should be used within about ten minutes of making up.

Average times of development: 16 minutes at 60°F. (15°C.), 11 minutes at 65°F. (18°C.), 7 minutes at 70°F. (21°C.).

Tap water is satisfactory for all solutions. The stock solution can be filtered if desired. Allow to stand for about 12 hours and then filter through a Whatman No. 2 filter paper.

When development is complete a short wash is given before fixing in an acid hardening and fixing bath (page 273).

All the physical developer formulae mentioned above suffer from two major disadvantages: they are extremely unstable and spontaneous precipitation of silver may occur immediately after mixing or at some time during the development process. Also, physical developers are very slow acting (see Table XXXV) and result in considerable loss in emulsion speed.

Recently, research workers at the Philips Research Laboratories in The Netherlands have discovered that the inclusion of two wetting agents (surfactants) in a physical developer greatly increases its stability to spontaneous precipitation of silver and also makes it possible to prepare more concentrated physical developers of higher activity than was previously possible.

#### 114.—STABILIZED PHYSICAL DEVELOPER

(*H. Jonker, A. Molenaar and C. Dippel*)

Metol	8.6 grams
Silver nitrate	1.7 grams
Citric acid, crystalline	21 grams
Armac 12D, 10% solution*	2 ml.
Lissapol N, 10% solution**	2 ml.
Distilled water to	1000 ml.

\*Surfactant, Dodecylamine acetate, Armour Industrial Chemical Co.

\*\*Surfactant, I.C.I. Ltd.

The silver nitrate content of the above developer can be increased by a factor of five with some loss in stability but a corresponding decrease in development time.

Formula 114 has a half life (the time after which the initial development rate is reduced by one half) of five hours, whereas a developer containing no surfactants has a half life of twelve minutes.

#### TANNING DEVELOPERS

It has already been mentioned elsewhere that in the process of development oxidation products are formed from the developing agents or substances, and these products have certain properties of varied interest and application in photography. We already know that they can affect the colour of the negative and stain fingers. They can also bring about the tanning of the gelatine of the emulsion—a process favoured by a low concentration of sulphite in the developer or, better still, by its complete absence. Under these conditions the tanning of the gelatine is proportional to the quantity of silver reduced. Hence the tanning is greatest in the most strongly blackened parts of the negative.

This property has been made use of in a number of ways in photography. In the preparation of tanned relief pictures for example the untanned gelatine, that is the gelatine

existing in the unexposed parts of the picture, is dissolved away by warm water. In certain processes of colour photography and in particular in the making of colour prints this process is of great importance.

In ordinary black-and-white photography the tanning effect on gelatine can be made use of in the following way. Wherever the gelatine has been tanned by the developer, the access of further developing solution to the film is rendered difficult and development slowed down. This braking effect on development is strongest in those parts of the negative which have received the heaviest exposure, that is in the highlights. Hence the further development of the highlights is held back, and a certain degree of compensation or equalising of contrast is attained; another point is that as the action of the developer is almost wholly on the surface of the emulsion, halation is not shown because the effects of halation occur in the depths of the emulsion to a very much greater extent than on the surface. Furthermore, such a developer tends to improve the acutance of the negative for the reasons explained on page 215.

The following formula are examples of tanning developers having properties such as have just been described.

#### 115.—TANNING DEVELOPER

Pyrocatechin	40 grains	2 grams
Sodium sulphite anhyd. solution 5%	2 drams	5 ml.
Caustic soda solution 5%	4 drams	10 ml.
Water to make	40 ounces	1000 ml.

Development time is 15-20 minutes.

#### 116.—TANNING DEVELOPER D175

Solution A.		
Pyrogallol		4 grams
Sodium sulphite anhyd.		5 grams
Water to make		1000 ml.
Solution B.		
Sodium carbonate anhyd.		28 grams
Water to make		1000 ml.
Mix equal parts solutions A and B immediately before use.		

With the exception of glycin most of the usual developing agents will produce a tanned image when used with a similar bath to the above, but pyrocatechin and pyrogallol are the most powerful tanning agents and should be first choice.

## CHROMOGENIC DEVELOPERS

The word chromogenic is applied to materials which when oxidised produce colours: its use in photography is comparatively recent, but is of material significance in the development of modern colour photography.

We have already seen that the oxidation products of developing substances have dyeing properties and can colour the silver image and stain gelatine, etc. Until recently this property was not utilised in practice to any great extent. Some small use was made of a brown-tone developer for lantern slides and papers, and was generally a pyrocatechin sulphite-free developer of the type described above.

Today this dye- or colour-producing property of developers assumes great importance, for the Kodachrome, Kodacolor, Agfacolor and other processes use this principle. The oldest example of the formation of a dye image by the development process is pyro, which in an alkali-rich formula does not produce a black silver image but one which is more or less brown or even yellow. If such a negative be treated with Farmer's reducer so that the whole of the silver image is removed, there still remains a clearly perceptible dye image of yellow-brown colour.

Starting from this point, Homolka sought materials which could act not only as developers but also as stepping-stones to dye products, and he found such compounds in indoxyl and thioindoxyl, which are capable of developing the latent image in exposed photographic materials and are oxidised by the development process to the deeply-coloured indigo dyestuffs.

The next step in the process was supplied by the researches of Fischer and Siegrist who discovered that many usable developers had the property of forming dyestuffs under the influence of the developed image. *p*-Phenylenediamine, *p*-aminophenol and allied compounds possess this property to a remarkable degree, and are able through simple oxidation with phenols and amines to produce a whole range of dyestuffs which are known as indophenols, indoanilines and indamines.

The oxidation which brings about the formation of these dyestuffs can be easily effected by the exposed silver bromide in the photographic film. Hence it is possible by direct development to obtain a reduction of silver and a proportional

formation of dyestuff, given, of course, that the dyestuff is insoluble in water and remains precipitated where it is formed, thus producing a dye image.

The phenols and amines used with the developers are called couplers because they couple with the oxidised developer to give dyestuffs. By the choice of suitable and specific couplers a very big range of compounds has been produced, many of them the subject of patents, but the work of the researchers already named has provided quite a number of valuable and useful couplers.

The origin and character of the colour depends in large degree on the developer and by the introduction of colour-deepening groups it is possible to produce a range of shades. For example, using dichloronaphthol as coupler and varying the developer from paraphenylenediamine to some of its derivatives one can obtain the shades in Table XXXVI. Of these three developers the third is perhaps the most easily obtainable and finds a place in many chromogenic developers. The diethyl compound of p-phenylenediamine is similar in its action to p-phenylenediamine itself.

The wide variety of colour tones obtainable through the particular choice of developer and coupling body is of great importance in the application of the method for colour photography, particularly in the preparation of separation pictures in the correct basic colours.

The great importance of such developers and couplers in colour photography will be obvious. There is also an interesting and fascinating field in the development of lantern slides and of positives on paper, for not only can one obtain a big range of colours by the choice of developer and coupler, but one can also remove the silver image in part or entirely by the use of Farmer's reducer.

#### XXXVI.—CHROMOGENIC DEVELOPER SUBSTANCES AND COUPLERS

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Using 2,4-Dichloro-alpha-naphthol.	
p-Phenylenediamine	Blue-red or violet
o-Methyl-p-phenylenediamine	Blue
N,N-Diethyl-p-phenylenediamine	Blue-green
Using N,N- Diethyl-p-phenylenediamine.	
Alpha naphthol	Blue
2:4-Dichloro-alpha-naphthol	Blue-green
Pentabromnaphthol	Green
p-Nitrobenzylcyanide	Yellow
1-Phenyl—3-Methyl—5-pyrazolone	Red

---

Colour developers can be used on most, but not all, lantern plates and papers. Chlorobromide papers are suitable, but bromide papers may not give very satisfactory image tones and chloride papers tend to show stained whites. In general it is more satisfactory to develop, fix and wash in the usual way, and then to bleach with a ferricyanide-bromide bleach and re-develop with the colour developer. This method is, of course, applicable to any type of paper.

#### 117.—FOCAL COLOUR DEVELOPER

N,N-Diethyl-p-phenylenediamine

-hydrochloride or -sulphate or

-bisulphite

	40 grains	2 grams
Sodium carbonate, anhydrous	1½ ounces	30 grams
Sodium sulphite, anhydrous	20 grains	1 gram
Potassium bromide	20 grains	1 gram
Hydroxylamine hydrochloride	20 grains	1 gram
Water to make	40 ounces	1000 ml.

It is advisable to prepare this developer from 10% stock solutions of the various ingredients before use. The colour formers are added immediately before use.

#### MAGENTA COLOUR FORMER

p-nitrophenyl acetonitrile	10 grains	0.5 gram
Acetone	½ ounce	12 ml.
Methylated spirit (colourless industrial)	4 ounces	100 ml.

#### BROWN COLOUR FORMER

2.5-dichloro acetoacetanilide	10 grains	0.5 gram
p-nitrophenyl acetonitrile	10 grains	0.5 gram
Acetone	½ ounce	12 ml.
Methylated spirit (colourless industrial)	4 ounces	100 ml.

#### BLUE COLOUR FORMER

Alpha-naphthol	14 grains	0.7 gram
Methylated spirit (colourless industrial)	4 ounces	100 ml.

#### BLUE-GREEN COLOUR FORMER

2:4-Dichloro-alpha-naphthol	20 grains	1 gram
Methylated spirit (colourless industrial)	4 ounces	100 ml.

#### GREEN COLOUR FORMER

2.4-dichloro-alpha-naphthol	10 grains	0.5 gram
2.5-dichloro acetoacetanilide	10 grains	0.5 gram
Methylated spirit (colourless industrial)	4 ounces	100 ml.

#### YELLOW COLOUR FORMER

o-Chloro acetoacetanilide or		
2.5-dichloro acetoacetanilide	20 grains	1 gram
Methylated spirit (colourless industrial)	4 ounces	100 ml.



For use take about 2 drams (10 ml.) of the colour former solution as detailed above for each 4 ounces (100 ml.) of developer solution. By mixing the colour former solutions nearly any shade of colour can be obtained. When once used, the developer must be thrown away and a fresh portion used for each separate development.

## TROPICAL DEVELOPERS

With any normal developer, increase of temperature means increased rate of development and increased danger of fogging, but the greatest danger is that at high temperature the gelatine of the emulsion swells excessively and becomes very weak and may even melt entirely. The name "Tropical Developer" is given to those formulae in which provision has been made to avoid dangerous swelling, either by the addition of a substance which reduces the swelling of the gelatine or by balancing the ingredients, eliminating those which cause swelling to excess. In general, the more alkaline the developer the more the gelatine swells and the more rapidly development takes place. Alkali free developers of the amidol type or one of the mildly alkaline fine grain developers are basically preferable to those with normal alkali content when working at high temperatures. The choice of a suitable developer formula is not, however, the only means of coping with high temperatures. There are a number of other techniques which can be used alone or in combination with a special formula.

## PRE-HARDENER

A very efficient method to prevent excessive swelling of the gelatine in a developer is the use of a pre-hardener solution.

### 118.—PRE-HARDENER

#### *Solution 'A'*

Formaldehyde, about 37% solution by weight	5	ml.
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#### *Solution 'B'*

Water	900	ml.
*0.5% solution of Anti-Fog No. 2 (6-Nitrobenzimidazole nitrate)	40.0	ml.
Sodium sulphate, desiccated	50.0	grams
Sodium carbonate, monohydrated	12.0	grams
Water to make	1000	ml.

\*To prepare a 0.5% solution, dissolve 1 gm. of Kodak Anti-Fog No. 2 in 200 ml. of distilled water.

The working solution should be prepared just before using by adding 5 ml. of Solution A to 1 litre of Solution B and mixing thoroughly.

Immerse the exposed film in the Pre-hardener for 10 minutes with moderate agitation. Then remove the film from the solution, drain for a few seconds, immerse in water for 30 seconds, drain thoroughly and immerse in the developer. The selection of the proper developer will depend upon the contrast and the time of development desired. In general, up to 90°F. (32°C.), conventional developers such as Formula 6, may be used without modification.

Times of development will be about as follows:

At 75°F. (24°C.)—use the normal development time recommended at 68°F. (20°C.) without pre-hardening

At 80°F. (27°C.)—85 % of normal time

At 85°F. (39°C.)—70 % of normal time

At 90°F. (32°C.)—60 % of normal time

At 95°F. (35°C.)—50 % of normal time.

Following development, rinse, fix in an acid hardening fixing bath, wash, and dry in the usual way.

#### AT HIGHER TEMPERATURES

At temperatures above 95°F. (35°C.), increase the concentration of Anti-Fog No. 2 in the prehardener up to double the normal formula concentration, if necessary, to control fog. Process as before, using a low-activity developer, such as a fine grain formula, to avoid excessively short development times. The average development time at 110°F. (43°C.) after prehardening is about one-quarter of the time necessary at 68°F.

In case the development time at elevated temperatures is too short for practical use, sodium sulphate can be added to the developer to extend the time of development. The keeping properties are adequate for ordinary tray and tank practice. Gradual deterioration does occur on standing, but the bath will keep satisfactorily (without use) in a closed bottle for 3 or 4 weeks at 95°F. (35°C.). For most applications, the useful life without replenishment is more than forty 8 × 10-inch films per gallon. Up to this usage no serious change in properties occurs.

## ADDITION OF SODIUM SULPHATE

The substance usually added to developers to reduce the swelling of gelatine is sodium sulphate (Glauber salt). It is essential that it should be present in high concentration. Most normal developers may be made suitable for tropical processing by the addition of 8 ozs. (105 gms.) of sodium sulphate cryst. to each 80 ozs. (1000 ml.) of the working solution. The time known to produce a certain gamma value at 68°F. (20°C.) or 65°F. (18°C.) in a normal non-sulphated developer, should be referred to in columns 1 or 2 in Table XXXVII and the required development time will be found in the appropriate temperature column for the same developer after the addition of the sulphate.

## SPECIAL TROPICAL DEVELOPER FORMULAE

Several special formulae for tropical developers are given in Table XXXVIII. Most of these formulae contain sodium sulphate while the alkali content is kept low or a milder alkali is used. Approximate developing times for the formulae are 5-7 min. at 24°C., 4-6 min. at 27°C., 3-4 min. at 29°C. and 2-3 min. at 32°C. These times are for tank development; for tray development, they have to be reduced by about one-fifth.

Where still higher temperatures have to be dealt with the use of the above pre-hardener, in conjunction with a tropical developer, is necessary. By this method developing can be carried out up to temperatures of 105°F. (41°C.).

After development a stop-bath of the type given in Formula 180 should be used. This has a hardening and anti-swelling effect. For fixing, too, a special tropical formula, such as Formula 187, is recommended.

## LOW-TEMPERATURE DEVELOPMENT

It is generally assumed that most developing agents become inactive below a temperature of about 12°C. (55°F.). It is advisable to avoid processing at such a low temperature but there may be cases where it is not possible to warm solutions to the normal temperature.

The feasibility of processing at very low temperatures has been investigated by R. W. Henn and J. I. Crabtree of the Kodak Research Laboratories (Communication No. 1019) who have shown that it is indeed possible to develop films at

**XXXVII.—DEVELOPMENT TIMES IN NON-SULPHATED  
AND SULPHATED DEVELOPER**

<i>Normal Development Time (minutes) in non-sulphated developer at:—</i>		<i>Calculated Development Time (minutes) in sulphated developer</i>				
65°F. (18°C.)	68°F. (20°C.)	75°F. (24°C.)	80°F. (27°C.)	85°F. (29°C.)	90°F. (32°C.)	
4	3½	4	3	2	1½	
5	4	5	3½	2½	1¾	
6	4½	6	4½	3	2¼	
8	6½	8	6	4	3	
10	8	10	7	5	3½	
12	9½	12	8½	6	4¼	
15	12	15	11	8	5½	
20	16	20	14	10	7	
25	20	25	18	13	9	

**XXXVIII.—SPECIAL DEVELOPERS**  
*Tropical*

	119 D13	120 DK15	121 DK15a	122 AN64	123 G222
Metol	—	5.7	5.7	2.5	2
Sodium sulphite anhyd.	52.5	90	90	25	50
Hydroquinone	10.5	—	—	6.5	5
Para-aminophenol hydrochloride	5.2	—	—	—	—
Sodium carbonate anhyd.	50	—	—	13.5	—
Potassium carbonate	—	—	—	—	30
Kodalk	—	22.5	5	—	—
Sodium sulphate	45	45	45	—	45
Potassium bromide	—	1.9	1.9	1	1.5
Special addition	Pot. iodide 2.1	—	—	—	—
Water to	1000	1000	1000	1000	1000
Development time (min.)	6-7 29°C.	2-3 32°C.	2-3 32°C.	2-3 29°C.	2 29°C.

low temperatures with modifications of standard formulae and even at very low temperatures with special developers of exceedingly high energy.

The main problem is, of course, the loss of activity of the developer. It is advisable therefore to start with a developer which at normal temperature is very active. For instance, a caustic hydroquinone developer (Table XXIII) or a still more alkaline variation of a caustic M.Q. developer (Formula 124), such as the following:

**124.—HIGH ENERGY DEVELOPER**  
*for low temperature processing*

---

Water (125°F. or 52°C.)	500	ml.
Metol	14	grams
Hydroquinone	14	grams
Sodium sulphite anhyd.	52.5	grams
Sodium hydroxide	17.6	grams
Potassium bromide	8.8	grams
Benzotriazole	0.2	grams
Add cold water to make	1000	ml.

---

For use down to +30°F. (1°C.): Use above formula undiluted.  
For use down to +5°F. (−15°C.): Take 3 parts stock solution, 1 part ethylene glycol. The ethylene glycol should be added prior to storage at low temperatures.

For very low temperature processing a caustic solution of two powerful developing agents has been designed, namely Amidol and Pyrocatechine.

**125.—AMIDOL-PYROCATECHIN DEVELOPER**  
*for very low temperature processing*

---

<i>Solution A</i>		
Water (125°F. or 52°C.)	500	ml.
Sodium bisulphite	100	grams
Amidol (2, 4 diaminophenol hydrochloride)	40	grams
Pyrocatechin	40	grams
Benzotriazole	2	grams
Add cold water to make	1000	ml.
<i>Solution B</i>		
Cold water	500	ml.
Sodium hydroxide	120	grams
Potassium bromide	20	grams
Potassium iodide	4	grams
Add cold water to make	1000	ml.

---

For use down to +30°F. (1°C.): Solution A, 1 part; Solution B, 1 part; Water, 2 parts.

For use down to +5°F. (−15°C.): Solution A, 1 part; Solution B, 1 part; Water, 1 part; ethylene glycol, 1 part.

For use down to −40°F. (−40°C.): Solution A, 1 part; Solution B, 1 part; ethylene glycol, 2 parts.

The glycol may be divided and added to each of these solutions previous to storage at low temperatures. Combine Solutions A and B only immediately before use, since the mixed developer oxidises rapidly. Solution A may also deteriorate on keeping, and should be kept well-stoppered and as cool as possible.

#### DEVELOPMENT OF THICK EMULSION LAYERS

Very thick emulsions known as *nuclear-track emulsions* are used in the recording of radioactive-particle tracks in for example the research of cosmic rays, biology, medicine and minerals.

The processing of these emulsions, which may be as thick as 1200  $\mu\text{m.}$ , does present some difficulty in ensuring that there is uniform development throughout the layer and that the emulsion is not distorted.

For emulsions up to 100  $\mu\text{m.}$  thick a conventional developer such as ID 19 (Formula 21, page 178) may be used if diluted to ten times its normal working strength. Processing of these thick emulsions does take a long time and the following technique is recommended by Ilford Ltd. Firstly the emulsion is given a pre-wash in distilled water for 20 minutes at 20°C. and then developed for up to one hour at 20°C. giving uniform gentle agitation. The exact time of development depends upon the nature and the thickness of the emulsion layer. Following development the emulsion is immersed in a 1% solution of acetic acid as a stop bath for ten minutes at 20°C. During this stage any surface fog of silver is removed by gentle rubbing with cotton wool. Fixing is carried out in a plain 30% hypo solution for two hours at 20°C. using gentle agitation and followed by washing for four hours in running water. To avoid the possibility of distortion by heat, it is best to dry the emulsion using circulating air and to gradually reduce the relative humidity of the air.

For emulsions thicker than 200  $\mu\text{m}$ . two techniques may be used to ensure even processing without distortion. These are the *temperature cycle* and *constant low temperature* or *isothermal* methods. Both these methods require a specially formulated developer such as the "Brussels" formula (No. 126) shown below.

**126.—DEVELOPER FOR NUCLEAR TRACK EMULSIONS**  
*"Brussels" formula*

Sodium sulphite, anhyd.	18 grams
Potassium bromide	0.8 grams
Boric acid	35 grams
Amidol*	4.5 grams
Distilled water to make	1000 ml.

\* Add the amidol to the remainder of the solution immediately before use.

In the temperature cycle method the emulsion is given a pre-soak in distilled water for fifty minutes, during which time the water temperature is gradually reduced from 20°C. to 5°C. This is followed by soaking in the "Brussels" Amidol developer for fifty minutes at 5°C. to allow the developer to be absorbed throughout the layer without development taking place. To develop the layer remove it from the developer solution, blot off any surface liquid and allow to warm to 25°C. at about 1°C. per minute for fifty minutes.

Development is stopped by immersion in a dilute solution of acetic acid for fifty minutes whilst slowly cooling to 5°C. To minimize the risk of bleaching of the silver image, fixing is carried out at 5°C. using a 30% hypo solution containing 8 grams per litre of silver.

Washing is achieved by allowing change of about 3% of the total volume of the solution per hour and at the same time raising the temperature to between 10° and 15°C. This washing procedure may take several days and must be very carefully controlled.

Drying of these very thick emulsion layers must be carried out very slowly and is best accomplished by successive immersion in alcohol/water solutions of gradually increasing alcoholic content. The final solution containing 90% alcohol, 5% glycerine and 5% water. The times of immersion are gradually lengthened from two and a half hours to eight hours in the

last solution. Finally the emulsion is allowed to dry in air at 55% relative humidity.

In the isothermal method the pre-soaked emulsion is cooled to nearly 0°C. and development takes place at this temperature for as long as several days, depending on the thickness of the layer.

Table XXXIX summarises these two commonly used processing procedures for nuclear-track emulsions. Additional information can be found from the data sheet supplied by the film manufacturer.

**XXXIX.—FILM PROCESSING PROCEDURES FOR NUCLEAR TRACK EMULSIONS**

	100 $\mu\text{m.}$ (microns) 20°C.	$\geq 200 \mu\text{m.}$ (microns)* temperature cycle
1. Pre-soak (distilled water)	20 min.	50 min. 20° → 50°C.
2. Develop	1D 19 (No. 21), 1 + 9, 15–70 min.	(i) No. 126, 50 min. (7 hrs.), (ii) $\frac{1}{2}$ hr. (1 hr.) 5° → 25°C.
3. Stop	1% acetic acid 10 min.	0.2–1% acetic acid, 50 min. (7 hrs.) 25° → 5°C.
4. Fix	30% hypo 2 hrs.	30% hypo $1\frac{1}{2} \times$ clearing time 5°C.
5. Wash	4 hrs.	hrs. (days) 10–15°C.
6. Dry	air	alcohol/water

\* The exact times depend upon emulsion thickness. Times quoted are for 200  $\mu\text{m.}$  (and 1000  $\mu\text{m.}$ ) emulsions.

#### QUICK-FINISH (RAPID ACCESS) DEVELOPERS

There are numerous applications of photographic methods where it is important that development shall be as rapid as possible. The normal cycle of processing, even if it is reduced to a few minutes only, is too long for many purposes. This is for instance the case in one of the most important applications of high speed processing, namely the recording of cathode ray tube traces, particularly in radar work. When an



aeroplane is detected by the radar devices, it may be essential that the information should be passed with the minimum of delay to the control station. Seconds or even fractions of seconds can be of highest importance.

Another valuable use of high speed processing is in the recording of instrument dials, to enable the inspecting personnel to examine the exposed film or paper as soon as possible after recording. A well-known application of high speed processing is the photo finish method which takes a photograph at the end of a race and supplies a print within about 1 minute.

In all these cases highly active developers are required and the formulae such as those in Table XL make full use of all means to accelerate the developing process, such as high general concentration, strongest alkali (sodium hydroxide) at maximum content and also high temperature. In cases where temperatures are employed considerably exceeding normal working temperatures special "Quick-Finish" (rapid access) films have to be used which stand temperatures up to nearly 200°F. (93°C.). The emulsions of these films are specially hardened and also thinly coated. It is in fact possible to develop these films in the short period of one-fifth of one second, but this requires, of course, the use of special high speed processing machines in which the developing, fixing and washing solutions are pumped on to the film, picture by picture, and are almost instantly blown away again by a jet of compressed air so that the next stage of processing can be applied.

In normal photographic practice one will be satisfied with the developing times of a few seconds. Using a developer such as Formula 128 in Table XL, for instance, a normal film would require a developing time of 20-30 seconds at 70°F. (21°C.), while a "Quick-Finish" film requires only 15 seconds under the same conditions. For the processing of this special film higher temperatures can be applied and the developing time can thus be reduced to, for instance, 4 seconds at 110°F. (43°C.).

## TWO-BATH DEVELOPMENT

In the ordinary process of development the developing agent becomes used up and various reaction products, particularly

bromides, slow the action of the bath. To meet these conditions it is necessary to increase time of development or to add a replenishing solution. There exists another method of overcoming these difficulties, and that is the use of separate baths for the developing agent and the alkali, or, as it is generally called, two-bath development.

The first bath contains only the developing agent and the preservative, and therefore no, or only incomplete, development takes place in it. What happens is that the exposed film or plate becomes saturated with the solution. As no chemical action takes place, the properties of the bath do not alter; all that happens is that each plate or film treated in it removes a small quantity of the solution when taken out. Hence such a bath, being constant in properties, allows very constant results to be obtained. As the concentration of such a bath can be altered at will, so can the desired grade of contrast in the negative be influenced within comparatively wide limits and where one type of material is being used the optimum conditions can be obtained and maintained.

**XL.—SPECIAL DEVELOPERS**  
*Quick-Finish*

	127 <i>C. Orlando Phot. Sc. Eng. 2, 144</i>	128 <i>L. S. Fort- miller and co-operators Phot. Eng. 7, 17</i>	129 <i>G. E. Duffy Phot. Eng. 6, 127</i>	130 <i>D8</i>
Alcohol	—	—	50	—
Metol	13	5	14	—
Sodium sulphite anhyd.	80	90	52	90
Hydroquinone	26	45	14	45
Sodium hydroxide	26	40	27	37.5
Potassium bromide	—	10	8.8	30
Benzotriazole 1%	200	25	200	—
Water to	1000	1000	1000	1000
Dilution	—	—	—	2:1
Development time (sec.)	0.2 185°F.	1 140°F.	0.2 170°F.	2 min.

The actual development takes place in the second bath which contains the alkali: here chemical action takes place but not in quite the same degree as in a normal developer. The film is already swollen and saturated with fresh developer solution and the process of development is therefore speedy and complete. Moreover, as the bath only contains alkali it is cheap and can be renewed at frequent intervals.

The two-bath method has other advantages, one of which is that a large tank can be used for the developing agent solution, but a small one for the alkali. The method is worthy of more attention than it has hitherto received.

### 131.—TWO-BATH DEVELOPER

1. Metol	100 grains	5 grams
Hydroquinone	40 grains	2 grams
Sodium sulphite, anhyd.	4 ounces	100 grams
Sugar (cane)	4 ounces	100 grams
Sodium bisulphite	100 grains	5 grams
Water to make	40 ounces	1000 ml.
2. Sodium sulphite, anhyd.	4 ounces	100 grams
Sodium carbonate, anhyd.	200 grains	10 grams
Water to make	40 ounces	1000 ml.

The addition of sugar and bisulphite to the first bath has the effect of retarding the action of the bath and at the same time preventing the appearance of any image due to the slight alkalinity of the sulphite.

The negative material should have about 5 minutes in solution 1, and 4-6 minutes to develop in solution 2.

### 132.—TWO-BATH FINE-GRAIN DEVELOPER (H. STOECKLER)

1. Metol	100 grains	5 grams
Sodium sulphite, anhyd.	4 ounces	100 grams
Water	40 ounces	1000 ml.
2. Borax	200 grains	10 grams
Water	40 ounces	1000 ml.

The time that films should remain in solution 1 varies with different makes of film; the times for the film groups as given on page 38 are as follows (at a temperature of about 65°F. or 18°C.):

Group A	3 mins.
Group B	4 „
Group C	6 „

The development time in the second bath is about 3 minutes and applies to all makes of film.

H. Stoeckler sets out the advantages of the two-bath fine-grain developer method as follows: (1) Harmonious compensation for great contrasts when used for the new and harder films, soft negatives of a gradation which allows easy enlarging. (2) The effective sensitivity of the film is not materially reduced. If it is imperative not to lose any sensitivity, only the first bath should be used and the development carried out for sixteen minutes. (3) As it is development at the surface, there is less halation and irradiation, and the best possible rendering of sharpness. (4) Great economy and cheapness of the solutions, which last longer and can be used many times.

### 133.—TWO-BATH KODAK DK20 SUPER-FINE GRAIN DEVELOPER

1.	Water distilled at 125°F. (52°C.)	15 ounces	750 ml.
	Metol	45 grains	5 grams
	Sodium sulphite, anhyd.	2 ounces	100 grams
	Potassium thiocyanate	8 grains	1 gram
	Potassium bromide	4 grains	0.5 gram
	Distilled water to	20 ounces	1000 ml.
2.	Kodak	175 grains	20 grams
	Water (distilled)	20 ounces	1000 ml.
3.	Water distilled (about 125°F.)	15 ounces	750 ml.
	Metol	65 grains	7.5 grams
	Sodium sulphite, anhyd.	2 ounces	100 grams
	Potassium thiocyanate	44 grains	5 grams
	Distilled water to	20 ounces	1000 ml.

For use the solution 2 is diluted 10 times (50 ml. made up to 500 ml. with water). This is thrown away after using for the development of one film. The total bulk of solution 1 is kept at 1000 ml. by filtering back into the bottle after use. 20 ml. of Replenisher (solution 3) is added to the amount required for the tank for each film after the first. Development time is thus kept constant.

The following development times in minutes are correct for a gamma of 0.7 at 65°F. (See also page 38 for Film Groups:) Group A films: 6½ mins. in Bath 1, 3½ mins. in Bath 2; Group B films: 10 mins in Bath 1, 3½ mins. in Bath 2; Group C films: 15 mins. in Bath 1, 3½ mins. in Bath 2.

As already noted on page 235 the principle of two-bath development may be usefully combined with high speed development. The high speed two-bath developer meets the requirements of those who must complete the processing of exposed films in the shortest possible time. The following method permits processing within fifteen minutes.

### 134.—HIGH SPEED TWO-BATH DEVELOPER

1.	Hot water (125°F. or 52°C.)	30 ounces	750 ml.
	Metol	100 grains	5 grams
	Sodium sulphite, anhyd.	1½ ounces	30 grams
	Hydroquinone	200 grains	10 grams
	Water to make	40 ounces	1000 ml.
2.	Hot water (125°F. or 52°C.)	30 ounces	750 ml.
	Sodium carbonate	5 ounces	125 grams
	Water to make	40 ounces	1000 ml.

Solutions 1 and 2 are stored separately and used separately. Solution 2 must be replaced when it becomes badly discoloured. Both solutions are used at full strength.

For development immerse films for one minute in solution 1, agitating the whole time, then transfer film to solution 2 for one minute. The solutions should be used at a temperature of 70°F. (21°C.). If bath temperature be 75°F. (24°C.) then only 45 seconds should be given in each bath, but should bath temperature fall to 65°F. (18°C.) then development time in each bath must be 1 minute 15 seconds.

Contrast can be controlled by varying the time of immersion in solution 2 as contrast increases with increasing time of immersion in this solution.

As soon as development is judged complete plunge film into a stopbath consisting of a 1% solution of acetic acid.

### MULTI-SOLUTION TECHNIQUE

Multi-solution developer is made up of a range of concentrated stock solutions of good keeping quality, so that by simple measurement and without weighing, a whole selection of developers can be prepared easily and rapidly. This method has the advantage that when a particular developer is only wanted occasionally, or when one uses a range of developers such as a normal negative developer, a fine grain or a paper developer, one can prepare any or all such developers quickly and safely from the same stock solutions. If one has a normal developer in frequent use it will be necessary to keep it ready made up, but even then it is an advantage to have a multi-solution set at hand, either to allow rapid preparation economically and quickly of a special developer, or to use the stock solutions to modify the normal developer in some desired manner.

### 135.—METOL-HYDROQUINONE MULTI-SOLUTION DEVELOPER

<i>(A) Metol Stock Solution</i>		
Sodium sulphite, anhyd.	40 grains	2 grams
Metol	40 grains	2 grams
Water to make	4 ounces	100 ml.
<i>(B) Hydroquinone Stock Solution</i>		
Sodium sulphite, anhyd.	40 grains	2 grams
Hydroquinone	40 grains	2 grams
Water to make	4 ounces	100 ml.
<i>(C) Sodium Sulphite Stock Solution</i>		
Sodium sulphite, anhyd.	$\frac{3}{4}$ ounce	20 grams
Water to make	4 ounces	100 ml.
<i>(D) Sodium Carbonate Stock Solution</i>		
Sodium carbonate	400 grains	20 grams
Water to make	4 ounces	100 ml.
<i>(E) Potassium Bromide Stock Solution</i>		
Potassium bromide	200 grains	10 grams
Water to make	4 ounces	100 ml.
<i>(F) Borax Stock Solution</i>		
Borax	100 grains	5 grams
Water to make	4 ounces	100 ml.

The preparation of a developer with the aid of these stock solutions is shown by an example using the Focal Universal M-Q developer No. 16. To produce a dish developer with a dilution of 1 : 5 we shall require the following quantities taken in the order given.

<i>Focal Universal M-Q No. 16</i>	<i>Original Formula</i>	<i>Stock Solutions</i>	<i>Quantity for 600 ml.</i>
Metol	3 grams	150 ml. (A)	15 ml.
Sodium sulphite	75 grams	375 ml. (C)	37.5 ml.
Hydroquinone	11 grams	550 ml. (B)	55 ml.
Sodium carbonate	75 grams	375 ml. (D)	37.5 ml.
Potassium bromide	1 gram	10 ml. (E)	1 ml.
Water to make	6000 ml.	6000 ml.	600 ml.

Note that in each case the total volume of water is given and not the amount which must be added to reach the required volume. In the case of the third column of figures, for example, the total volume of the necessary stock solutions is 146 ml. We shall therefore require to add a further 454 ml. of water to bring the volume to 600 ml.

It will be seen that the developer compounded from the stock solutions is not quite identical with the original formula inasmuch as the stock solutions A and B each contain a certain amount of sodium sulphite as preservative. The increase in the total sulphite content is not sufficient

to call for any adjustment when the stock solution C is added.

From the example given it will prove a simple matter to make up other developer combinations using the multi-solution technique. There is just one precaution to bear in mind and that is not to overstep the saturation limit with the stock solution of any one constituent. (The saturation limit of all the chemicals can be obtained under the heading of "solubility" in the list on pages 411-416.)

## INORGANIC DEVELOPERS

Inorganic developing agents such as ferrous oxalate had been used in the early days of photography but were then completely superseded by the organic developers. However, recent inorganic developers employing a metal ion, such as iron or titanium, and a modern chelating (sequestering) agent give results comparable to conventional developers. As a matter of fact, they have many features of special interest.

Iron developers can be prepared by replacing the complex oxalate ion by more modern complexing agents, such as ethylenediaminetetraacetic acid (EDTA). The compound formed by mixing ferrous sulphate and EDTA is commercially available; in a 5 per cent solution it gives a developer which is an improvement on the old iron developers as it is faster working.

Still more promising results are obtained with titanium developers as they show a greater activity. To prepare these developers, titanium trichloride is used in the form of the commercial 20% solution. By combining this solution with EDTA as the chelating agent, a purple solution is formed which is a very active developer. As with the usual organic developers, it is necessary to adjust the pH value and to add anti-fogging agents. A formula of this type has been published by G. M. Haist, J. R. King, A. A. Rash and J. I. Crabtree:

### 136.—TITANIUM DEVELOPER

Titanium trichloride solution 20%	3 ounces	75 ml.
EDTA (tetra-sodium salt)	4 ounces	100 grams
Sodium acetate	350 grains	20 grams
Potassium bromide	70 grains	4 grams
Water to make	40 ounces	1000 ml.

The pH of the mixed solution must be adjusted to 4.0 with hydrochloric acid. The sodium acetate is added as a buffer and has no photographic effect. The developer has given good results with cine positive film at 5 minutes development (68°F.). It gives higher speed at shorter development time than conventional developers. For the development of negative films it may be advisable to dilute the developer and to increase the concentration of potassium bromide.

Inorganic developers offer the interesting possibility of regeneration by electrolytic methods. The above titanium developer can be regenerated by electrolysis at a current density of 250 amps per square metre in a cell having a lead cathode with a graphite anode enclosed in a porous cup. The exhausted developer is used as the catholyte and a dilute sulphuric acid solution as the anolyte.

#### RESTRAINED DEVELOPMENT

We have seen (page 77) that in addition to the chemical reaction involved in the reduction of the silver bromide there are other processes taking place during development which can notably influence the result. The process of image formation is considerably affected by the fact that in the heavily exposed areas the bromide set free during development acts as a strongly retarding agent on the growth of the image at those points. This naturally suggests that if we could control this particular process it could be used to modify the contrast of the negative. Actually such methods were published about 1900 and in recent years they have again been brought forward sometimes with somewhat extravagant claims as to their advantages.

One of the oldest of such processes by which the bromide effect is utilised is that which the Germans called "Planliege" development, literally "flat lying development". This consists in having the carefully levelled negative lying sensitive face up in developer which is completely undisturbed. The perfectly horizontal position of the plate inhibits the diffusion or flow of the exhausted developer from the heavily exposed parts of the negative with the natural effect that development slows down in the highlights but proceeds normally in the shadows. This never was a popular process with amateurs because of



the trouble involved in the careful levelling of the plate but it still finds applications in the graphic arts.

A simpler method makes use of the principle of intermittent development and was introduced about the year 1911. If a negative is plunged into developer and then withdrawn, the adsorbed developer continues to work but in the highlight areas its energy is soon spent. In the shadows or lightly exposed areas the developer retains sufficient strength to continue development for a longer period. The result is that development of the highlights is held back but the shadow areas go on developing. This can be of real advantage in the case of underexposed negatives or those of very contrasty subjects.

This principle can be applied in various ways. One of the oldest methods is to place the negative in developer until reasonably saturated with the developer solution, then withdraw it and place in water, repeating the process until the desired effect or degree of development has been attained. In later years this process had been investigated by A. Knapp who suggested the following formula.

#### 137.—AMIDOL DEVELOPER FOR INTERMITTENT DEVELOPMENT

Amidol	10 grains	0.5 gram
Sodium sulphite, anhyd.	40 grains	2 grams
Water to make	4 ounces	100 ml.

The negative is given three soakings in the developer for 40 then 50 and finally 90 seconds respectively and after each immersion in the developer is allowed to lie in water for two minutes without being disturbed.

More energetic and more concentrated developers may be successfully used but no hydroquinone developer is suitable.

H. C. McKay has proposed the following metol formula:

#### 138.—METOL DEVELOPER FOR INTERMITTENT DEVELOPMENT

Metol	$\frac{1}{2}$ ounce	15 grams
Sodium sulphite, anhyd.	2 ounces	60 grams
Caustic soda	90 grains	6 grams
Sodium carbonate	90 grains	6 grams
Borax	1 ounce	30 grams
Water to make	32 ounces	1000 ml.

Another method of intermittent development consists in taking the developer-saturated negative and pressing the gelatine face into close contact with a glass plate and then

leaving the two plates in water at a temperature of 70°F. (24-25°C.) until development is complete. This process was re-introduced under the name P. & H. process and a special film ribbon was provided to allow the development of roll films by the process.

The metol developer, Formula 138, is suitable for this P. & H. process, the negative being given an immersion ranging from 70 to 140 seconds according to the contrast of the subject and the properties of the film used. The greater the contrast the shorter the time the film should remain in the developer. Allow the film 15 minutes in the water.

Whilst intermittent development can provide the desired adjustment of contrast it would be quite wrong to think that there are no other methods of attaining a similar result. The method makes use of concentrated developer and hence there is a notable difference as compared to the result obtainable with normal developers. If one uses a soft compensating fine-grain developer almost the same result can be obtained as by the intermittent method, with the added advantage of consistent fine grain. Hence the practical value of intermittent development is open to doubt.

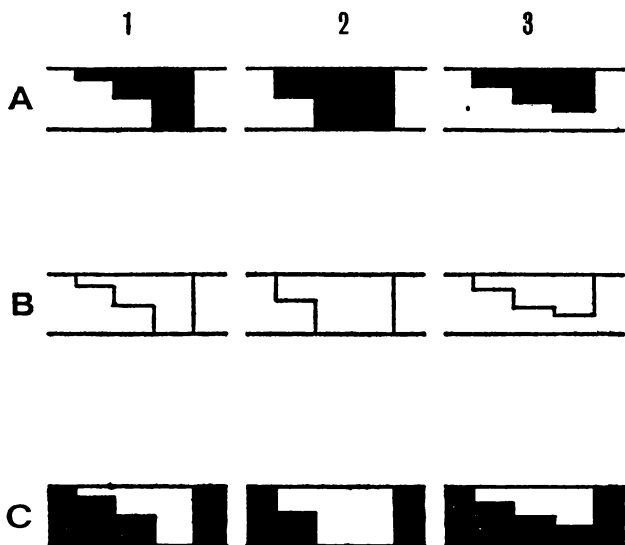
## REVERSAL DEVELOPMENT

The purpose of reversal development is the opposite of that of normal development in which from an exposed plate or film we obtain a negative, or if we are printing from a negative we get a positive. With reversal development there are two stages which result in our obtaining a positive direct from an exposed plate or film, or a negative from a negative and a positive from a positive by contact or enlarging methods of reproduction.

The process is of particular importance in the handling of cine-film and 35 mm. film for miniature cameras and finds wide application in many processes of colour photography. In cases where the amateur requires only a single copy of an exposure, reversal development will supply him with a transparency which can be visually examined or projected in a small projector. The process is also useful in the preparation of duplicate negatives.

Reversal development is not a simple process and does not permit any universally applicable formula being used,

## THE PROCESS OF REVERSAL DEVELOPMENT



Reversal development involves three distinct stages. **A.** Primary development in which the exposed material is developed with an energetic developer to a normal negative. The diagram shows a section through the three parts of the negative, shadows, middle tones and highlights. **B.** The dissolving of the primarily-developed silver. This is effected by a suitable silver solvent, leaving behind the unexposed silver bromide, which will go to form the positive image. **C.** This unexposed silver bromide is now exposed to light and developed to form the actual positive.

Column 1, on the left, shows the reversal development of a well exposed picture. Column 2, in the centre, shows the reversal of an over-exposed picture, the highlights of which are being lost. Column 3, on the right, shows the reversal of an under-exposed picture. The highlights of this under-exposed picture will remain partly undeveloped in stage A, leaving too much silver bromide undissolved in stage B, which exposed in stage C leads to much density in the highlights.

as its successful application depends to so large an extent on the nature of the sensitive emulsion being used.

The difficulties that may arise can best be dealt with by making a detailed study of the processes which comprise reversal development of black-and-white materials (see page 245):

- (1) The exposed material, plate or film, is first developed with a developer which will ensure that every exposed grain in the emulsion is developed. This is the primary development.
- (2) The image so developed is next dissolved completely away with a suitable silver solvent.
- (3) The silver bromide remaining, that is the silver bromide not affected by the first exposure, is now fully exposed and developed and so provides the final image; this is the secondary development.

It will be clear that the nature and quality of this final image will be determined by the quantity and structure of the silver bromide left behind after the removal of the primary silver image.

If that primary image was a dense one, extending well into the emulsion layer, then the silver bromide remaining after its removal would be comparatively thin, and the secondary image produced by its exposure and the secondary development would naturally be thin also.

If, on the contrary, the primary image was thin, then a large quantity of silver bromide would remain and would produce a dense and probably clogged-up image on secondary development.

If a successful result is to be obtained by the reversal process, it is obvious that a nice balance must be observed between the image produced by the first exposure and the quantity of silver bromide which will remain when the primary image is removed.

It must be noted therefore:

- (1) That the primary exposure will largely determine the density and the proportion of the emulsion forming the first image, and therefore the density and quality of the second or final image. Thus there is no room for either over or under-exposure and latitude in exposure when using the reversal process is small.

- (2) The development of the primary image will have a great influence on the result. Such development must be complete, and so a strong-working, energetic developer is used and development time is such that there shall be no doubt that full development has been attained. To further this end it is usual to employ a silver bromide solvent in the primary developer, such as ammonia or potassium thiocyanate which assists in the development and helps to reduce the silver bromide left for the secondary image.
- (3) When the primary development is complete the image so developed is dissolved away in what is usually called the bleach bath. After a wash the remaining silver bromide is fully exposed to white light and completely developed in a normal developer.

Any sensitive material can be reversal processed but those intended for it are specially coated for the purpose, and the emulsion is usually thinner than with ordinary films.

In the various formulae which follow, examples of most of the practical variations in reversal procedure will be given, but it must be emphasised that for any particular reversal film the maker's instructions should be adhered to, as they have been carefully worked out for that particular film.

#### XLI.—FIRST DEVELOPERS FOR REVERSAL PROCESSING

	139 D168	140 D19+ thiocyanate	141 ID36+ hypo
Metol	2	2	3
Sodium sulphite anhyd.	90	90	50
Hydroquinone	8	8	12
Sodium carbonate anhyd.	44.5	45	60
Potassium bromide	—	5	4
Potassium thiocyanate	2	2	—
Water to	1000	1000	1000
Dilution	0 1:1		1:1

Formula 139 (Kodak D168) is suitable for all Kodak continuous tone materials and formula 140 is suitable for Kodak Panatomic X film, whereas formula 141 requires different quantities of crystalline sodium thiosulphate (from 4-12 grams per litre) to be added to the diluted developer depending on the particular Ilford film being processed. Thus Fine Grain Safety Positive film requires the addition of 4 grams per litre, HP3 and HP4 requires 8 grams per litre and FP4 requires 12 grams per litre.

It is recommended that the user finds for himself the optimum quantity of thiosulphate to suit the particular film being processed. As a general guideline increasing the thiosulphate reduces the maximum and minimum densities that are obtained on reversal, i.e. the positive characteristic curve is displaced downwards to lower densities, whereas reducing the thiosulphate concentration has the opposite effect. Increasing the time of the first development has a similar effect to increasing the thiosulphate concentration.

#### **XLII.—BLEACH BATHS FOR REVERSAL PROCESSING**

	142	143 <i>Kodak R21A</i>
Potassium permanganate	4	—
Potassium dichromate	—	50
Water to	1000	1000
Sulphuric acid conc.	20	50
Dilution	—	1:9

*Caution* Add the concentrated sulphuric acid *slowly* with constant stirring to the *cold* solution of the permanganate or dichromate.

#### **XLIII.—CLEARING BATHS FOR REVERSAL PROCESSING**

	144	145 <i>Kodak R21B</i>
Sodium or potassium metabisulphite	25	—
Sodium sulphite anhyd.	—	50
Sodium hydroxide	—	1
Water to	1000	1000

# **XLIV.—SECOND DEVELOPERS FOR REVERSAL PROCESSING**

	146 D158	147 D8
Metol	3.2	—
Sodium sulphite anhyd.	50	90
Hydroquinone	13.3	45
Sodium carbonate anhyd.	69	—
Sodium hydroxide	—	37.5
Potassium bromide	0.9	30
Water to	1000	1000
Dilution	1:1	—

## **XLV.—REVERSAL PROCESSING** *Processing Steps and Formulae*

	Kodak	Ilford
1. First developer	D168 (No. 139) 5-10 min. Undiluted or 1:1, 20°C. Or No. 140 6 min. 20°C.	ID36 (No. 141) 12 min. 20°C. 1:1+Hypo
2. Wash	5 min.	3 min.
3. Bleach	R21A (No. 143) 3-5 min.	No. 142 3-5 min.
4. Wash		2-5 min.
5. Clear	R21B (No. 145) or 144 2 min.	Nos. 144 or 145 2 min.
6. Wash	$\frac{1}{2}$ min.	2 min.
7. Re-expose	2 $\frac{1}{2}$ min.	1-2 min.
8. Second Developer	D158 (No. 146) 2-5 min. 1:1, 20°C. Or No. 140 4 min. 20°C.	Same as first developer, 6 min. 20°C.
9. Wash	Rinse	Rinse
10. Fix	Acid hardening fix	Acid hardening fix
11. Wash	15-30 min.	30 min.

## REVERSAL OF PROCESS MATERIALS BY THE ETCH-BLEACH PROCESS

The etch-bleach process of reversal processing provides a simple and rapid method of preparation of reversals for positive working lithographic plates, photo-engraving, etc. In this process the silver image formed in the first developer is removed, together with the gelatine, by an etch-bleach bath (formula 148) to leave a positive relief image which can be developed or dyed to a particular colour.

### 148.—ETCH-BLEACH-BATH (Kodak EB-3)

- |    |                                       |          |
|----|---------------------------------------|----------|
| A. | Water, 86-95°F. (30-35°C.)            | 750 ml.  |
|    | Cupric chloride                       | 10 grams |
|    | Citric acid                           | 10 grams |
|    | Water to                              | 1000 ml. |
| B. | Hydrogen peroxide 10 volume solution. |          |

For use mix equal volumes of solutions A and B.

*Notes:* Hydrogen peroxide solutions tend to decompose on storage and this may result in incomplete removal of the gelatine although the silver image bleaches. If this occurs it is recommended that the proportion of hydrogen peroxide be increased.

### XLVI.—ETCH-BLEACH REVERSAL PROCESSING *For Process Materials such as Kodalith, Steps and Formulae*

1. First Developer	D8 (No. 147) + 4g./1 of potassium thiocyanate, 2½-3 min. 20°C.
2. Stop-bath	5% acetic acid, 15 seconds
3. Etch-bleach	EB-3 (No. 148)
4. Wash	15 seconds
5. Re-expose	
6. Second Developer	D158 (No. 146) or D8 (No. 147), 5-6 min. 20°C.
7. Hardener	see Tables LIII and LIV
8. Wash	5 min.

## ELECTROLYTIC DEVELOPMENT

The idea that electrolytic processes, which play so large a part in technology today might be of service in photography



is not new, yet so far no really practical method has been evolved although some interesting investigations have been carried out.

J. Rzymkowski has published a reproduction of an electrically-developed portrait, but did not disclose the composition of the developer solution. He used a cylindrical battery jar with a resistance between it and the electric light supply. In the battery jar a porous cell separated the anode from the cathode. The anode consisted of a metal plate, while the cathode was of cylindrical form and of punched metal. The film was placed round the wall of the battery jar. The time of development was given as 15 minutes with a current strength of  $\frac{1}{4}$ -ampere.

Another method which dispenses with electric current, but may be claimed as electrolytic, is that of R. S. Morse, who bathes the exposed material in the following bath and then places it in intimate contact with a copper plate.

#### 149.—BATH FOR ELECTROLYTIC DEVELOPMENT

Ammonia	1 $\frac{1}{2}$ ounces	40 ml.
Formaldehyde	85 minims	5 ml.
Mercuric chloride	10 grains	0.5 gram
Water	8 ounces	200 ml.

#### BASIC FORMULAE

The photographer can choose from a truly formidable collection of developer formulae. We have made every effort to arrange them in groups according to their properties and their modes of application. It should therefore not be unduly difficult to choose the right developer for any job. However in addition to the developers listed here the photographer is confronted by a host of formulae published elsewhere.

Through the publication of curves and data for every single recipe or formulae the impression is strengthened that essential differences do exist between all of them and that the results published in such detail are really a scientific contribution and that the photographer is expected to keep strictly to all these recommendations.

In fact, on more close scrutiny we find, behind the overwhelming variation of formulae, repetition of the same basic concepts; in many cases old formulae are named and coded

in a manner which can suggest a new formula and the claim for original authorship. This situation leads to the question whether such a vast variety of formulae is really necessary.

When analysing in detail the formulae as grouped in the various tables of this book it soon becomes obvious that those in each of the groups are in fact very closely related.

It seems therefore to be quite feasible to devise in most cases a formula which represents all the main features of the group in question. An attempt to devise such basic formulae has been made in Table XLVII. These formulae are not merely of academic interest but may be used in practice to produce very satisfactory results.

Formulae published by various manufacturers of sensitive material are certainly primarily designed for their own makes. However, this does not mean that these formulae are not interchangeable. Only highly specialised formulae must be restricted to the use of the product for which they have been originally evolved.

## DESENSITISING

Desensitising is a process which reduces the light sensitivity of emulsions to such a degree that they can be developed in comparatively bright light. The process was discovered by Dr. Lупpo Cramer and is no doubt one of the most interesting photochemical effects from the theoretical point of view. For some time it was of great practical importance too as it allowed panchromatic and other high speed materials to be handled under conditions which permitted closest possible control.

Today, however, the process is only of very limited practical importance, because development is generally carried out by the time-temperature method.

The main present-day use of desensitisers is in developing high speed emulsions by direct inspection, as by the intermittent development method described on page 243. In cases where special effects are required, direct control of the negative image in the developer can be advantageous too. Yet again, close inspection of the image during development might help to save negatives where there are serious doubts as to the correctness of exposure and it may be necessary to

**XLVII.—“BASIC” DEVELOPER FORMULAE\***

	<i>General purpose developers</i>			153 <i>Fine Grain</i>	<i>Special developers</i>			157 <i>Rapid contrast</i>
	150 <i>Soft</i>	151 <i>Normal</i>	152 <i>Contrast</i>		154 <i>Tank</i>	155 <i>High contrast</i>	156 <i>Rapid</i>	
Metol	1.5	1	0.5	2	1	2	15	—
Sodium sulphite anhyd.	10	25	20	100	40	60	50	90
Hydroquinone	—	2	2.5	5	2	8	15	30
Sodium carbonate anhyd.	8	10	10	—	10	40	—	—
Sodium hydroxide	—	—	—	—	—	—	10	20
Borax	—	—	—	2	—	—	—	—
Potassium bromide	0.5	0.5	0.5	—	0.5	4	8	10
Water to	1000	1000	1000	1000	1000	1000	1000	1000

\*For basic formulae using Phenidone-hydroquinone, see Table XXIX

modify development or even the developer itself to a large extent.

Desensitisers also prevent chemical fog caused by atmospheric action when films soaked with developer are exposed to air, which can happen in some types of developing machines. In this case the desensitiser acts as an anti-fogging agent.

Desensitising agents must be able not only to reduce considerably the light sensitivity of the silver halide but must do so without in any way affecting the latent image and without exerting any adverse effect on the developer and the developing process. Many such substances have been discovered but only a few have received practical application.

### *Phenosafranine*

This was the first densitiser to be used to any great extent, and appeared on the market under the names Pinasafröl and Desensitol. It is a useful desensitiser but has one drawback: it stains films and fingers. Nevertheless it is cheap, works well and is compatible with most developers.

An exception is hydroquinone, the action of which is accelerated. With normal M-Q developers there is little perceptible effect so long as the concentration of phenosafranin is low.

Désensitisers can be used in two ways, either as a fore-bath or added to the actual developer. Of these two methods the fore-bath is always preferable for a number of reasons, and should be employed whenever possible. Some of the desensitisers are precipitated by certain constituents in developers and can cause troublesome flecks and spots of colour on negatives and thus should not be used in the developer.

Desensitisers are best kept in the form of a stock solution which can be diluted when required to prepare the fore-bath.

#### 158.—PHENOSAFRANINE DESENSITISER

Phenosafranine  
Water

1 part  
1000 parts

When the fore-bath is required, one part of the stock solution is diluted with 10 parts of water, thus giving a bath of 1 : 10,000.

The bath can be used for several negatives, but should not be kept too long as moulds tend to grow on it.

When used in the developer the desensitiser should have approximately the same strength as in the fore-bath, hence for each 40 ounces of developer (1000 ml.), 4 ounces (100 ml.) of the stock solution will be used.

When the plate or film has been about one minute in the fore-bath or the developer, the yellow safelight can be turned on in the dark-room. This should be safe for all sensitive material, but if very highly-red-sensitive panchromatic material is being developed, then a somewhat darker yellow-green safelight may be preferable.

Basic scarlet N is another desensitiser, consisting of a mixture of phenosafranin and chrysoidine, the latter being a brown dyestuff. Its properties are similar to those of phenosafranin, except that it must only be used as a fore-bath. The following formula reproduces the properties of basic scarlet.

#### 159.—DESENSITISER (B. T. DENNE)

Chrysoidine	20 grains	1 gram
Phenosafranin	20 grains	1 gram
Distilled water	4 ounces	200 ml.
Alcohol	1½ drams	5 ml.

For use, one part of stock solution to 50 parts of water.

*Caution:* Many fine-grain developers will not work well with densitisers, which, therefore, should not be used with them.

### *Pinacryptol*

The disadvantage of the strong staining properties of phenosafranin soon led to the discovery of other desensitisers such as pinacryptol green. This desensitiser must be used as a fore-bath and not in the developer solution.

#### 160.—PINACRYPTOL DESENSITISER

Pinacryptol green	20 grains	1 gram
Water	20 ounces	500 ml.

To prepare the bath, 1 part of the above stock solution is diluted with 9 parts of water, giving a bath of 1 : 5000 of the actual desensitiser.

The material to be desensitised is given two minutes in the fore-bath, then the light safelight can be turned on, the plate or film quickly rinsed and placed in the developer.

## *Increasing Film Speed*

There are various means of increasing the speed of sensitive materials when extra sensitivity is required for special purposes. These methods can be classified as follows:

- (1) Treatment before exposure. This is known as hypersensitising, and increases the apparent speed of the material.
- (2) Treatment after exposure, but before development. This is known as latent image intensification, or latensification. It increases the sensitivity of the latent image to development, usually by increasing the size of the sensitivity specks by chemical or light treatment similar to hypersensitising.
- (3) Development with special high-energy developers.
- (4) Intensification of the developed negative. This is dealt with on page 347.

### HYPERSENSITISING

Hypersensitising was very useful when emulsions were generally considerably slower than they are now, but it is of little value with modern fast materials. These have already been hypersensitised during manufacture, and further hypersensitising by the amateur before exposure does not give good results. With careless handling it may even give rise to a great deal of fog and other troubles.

Nevertheless, materials cannot be hypersensitised sufficiently during manufacture to obtain the utmost sensitivity, because films and plates treated in the ways described below have rather poor keeping qualities. If these methods are employed, the material should be used within a few days of treatment.

The effect of hypersensitising is usually fairly uniform

over the range of colours to which orthochromatic films are sensitive, but it increases with the longer wave-lengths (redder colours of light) and is particularly pronounced in the infra-red region. Hypersensitising therefore affects pan films and plates more than others, and has special use in work with infra-red sensitive materials.

## BATHING

The commonest method of hypersensitising consists of bathing the film or plate in a dilute alkaline solution such as ammonia, borax, triethanolamine, or other amines. Alternatively a very dilute solution of silver nitrate or even plain distilled water may be used.

One of the effects of this treatment is that it dissolves out the slight excess of potassium bromide usually present in most emulsions. This potassium bromide increases the keeping qualities of the emulsion and keeps down fog, but it also decreases the speed, and this state of affairs is reversed by bathing. If silver nitrate solution is used, which not only dissolves out potassium bromide, but also provides free silver, the effect is even greater, but so is the fog.

When using the alkali solution which can be 1 part of 0.880 ammonia diluted with 30 parts of water, or a 0.5% solution of triethanolamine, the film is immersed in the solution in total darkness before exposure for two minutes at 55°F. (13°C.). The low temperature helps to minimise swelling of the gelatine. The excess liquid is then wiped off carefully, and the film dried as quickly as possible. The whole process is, of course, carried out in complete darkness. An anti-fogging agent such as a 1:30,000 solution of benzotriazole should be added to the developer during subsequent processing, to keep down fog.

## VAPOUR TREATMENT

In a second method of hypersensitising by chemical means the material is exposed to the vapour of such liquids as mercury. While the results are somewhat uncertain and inconsistent, this method does not require removal of the film from its wrapping as long as this does not contain metal. There is no wetting (and therefore no drying) of the film or

plate, and the colour sensitivity and curve of the material are unaffected.

Vapour treatment is best carried out by placing the film (which may be wrapped up with its backing paper, but removed from any metal reel or holder) in a non-metallic container which is tightly sealed. Alongside in the container, in a small dish, is put a drop of mercury. To observe and test the effect the material can be treated for a range of times of up to two days. As the container is sealed, it is soon filled with mercury vapour. Although the vapour pressure of mercury is very low at the temperature of this treatment, there is enough mercury vapour present to have an appreciable effect during the 24 to 48 hours for which the material is exposed to the vapour. It is believed that the vapour deposits mercury on the sensitivity specks in the emulsion, and increases the sensitivity of the film in this way.

#### FOGGING BY LIGHT

Apart from the chemical methods of hypersensitising, increased emulsion speed can be obtained by exposing the material to light for a very short time before the proper exposure. This increases the fog density and thus lowers the contrast of the image, which should just be apparent on development. The image density is, however, increased rather more than the fog density, resulting in an increased effective speed. Pre-flashing effectively extends the toe of the characteristic curve and gives a real speed increase. It also overcomes reciprocity failure if main exposure is long.

The procedure consists of pointing the camera, loaded with the films, at an evenly illuminated white card, and exposing with the smallest aperture and fastest shutter speed. The image of the card should completely fill the negative area, and it must be out of focus to avoid any image of the card texture. A certain amount of experiment will soon show the best conditions for any plate or film.

#### LATENT IMAGE INTENSIFICATION

This process, also known as latensification, is very similar to hypersensitising, except that it takes place after the exposure of the negative.



Bathing the material will give good results after exposure as well as before with the same solutions of alkalies, like ammonia, triethanolamine, etc. In addition, various oxidising agents can be used such as potassium permanganate, dilute nitric acid, and peroxide solutions. Aqueous sulphur dioxide solution has also been used quite successfully.

One such bath may be a 0.5% solution of potassium metabisulphite containing 0.85% of anhydrous sodium sulphite. This has a pH value (see page 88) of about 6. If the pH value is raised (the solution made more alkaline by decreasing the metabisulphite relative to sodium sulphite) the speed increase is greater, but so is the fog produced. If there is already too much fog, the bath must be made more acid by increasing the metabisulphite concentration, or some 1 : 30,000 solution of benzotriazole may be added.

The film is bathed, after exposure, in the solution for about five minutes at 65°F. (18°C.), well drained, and wiped carefully. To get the best speed increase out of the material, the film should not be developed immediately, but should be dried first (in the dark-room) before any processing is started.

This treatment after exposure instead of before has the advantage that there is no need to rewrap the material, and further, the loss of the anti-halo dye in the solution does not matter at this stage.

#### VAPOUR LATENSIFICATION

Mercury vapour can be used as for hypersensitising. The result is similar and just as uncertain. If anything, the speed increase is slightly greater with mercury vapour treatment after exposure in the camera than before.

Other vapours, such as those of formic and acetic acid, can also be used. They tend to soften the film base, so films should not be exposed to the vapour for too long.

Sulphur dioxide gas is also effective and can be used either in solution, as described above, or in the following way:

A dish or jar containing 1 ounce (25 ml.) of 10% acetic acid and 1 ounce (25 ml.) of 10% sodium sulphite (anhydrous) is placed in a light-tight tin. The exposed film is wound into a developing tank spiral, which is suspended above the dish in the tin. This is left for 24 hours and the film then developed as usual.

## POST-EXPOSURE FOGGING

Fogging by light after exposure can also increase the effective film speed. While with hypersensitising a very short exposure to a comparatively strong light is given, fogging after the camera exposure yields the best results with long treatment by a very dim light. Light of very weak intensity is much more effective in increasing an existing latent image than in starting a new one. Consequently the increase in the image density will be greater than in the fog density, and the shadows will be strengthened, but overall contrast decreased.

The film is exposed to a very weak dark-room light for about 30-60 minutes. For supersensitive panchromatic materials a dark green (Wratten Series 3) safe-light with a 10-watt bulb and a working distance of about 12 feet is best.

The speed increase obtainable by fogging after exposure is usually somewhat greater than by pre-exposure treatment (about 100%, as compared with 50-75%).

## HIGH-ENERGY DEVELOPMENT

This is perhaps the simplest and most convenient method for obtaining maximum emulsion speed. It does not need special apparatus or extensive modifications in processing technique. Its chief drawback, however, is rather coarse grain, since the characteristics of high-energy development formulae are the exact opposite of fine-grain developers.

Research by Kodak has shown that under certain conditions the addition of hydrazine salts or hydrazine derivatives such as semicarbazide hydrochloride results in greatly increased contrast and film speed. Such compounds can be added to a normal M.Q. developer like D72 or D19, in fact the SD19a formula given below is obtained by adding a small quantity of hydrazine dihydrochloride and an anti-fogging agent to the normal D19 developer.

The speed increase in this type of developer has been shown to be due to chemical fogging of silver halide grains. Only those silver halide grains adjacent to exposed grains are affected and not the under-exposed latent image, nor the other unexposed silver salts. The resultant disadvantage of this is, in addition to the graininess already mentioned, appreciable loss of definition in the developed silver image,

as the image is spread beyond what is recorded on the films by the camera lens. Mechanical defects such as finger marks, abrasion marks, and emulsion or agitation irregularities are also considerably magnified. Handle the film with care.

#### 161.—KODAK SD19a HIGH-ENERGY DEVELOPER

A. 6-nitrobenzimidazole nitrate,			
0.2% solution	385 minims	20	ml.
Hydrazine dihydrochloride	30 grains	1.6	grams
Water to make	1 ounce 100 minims	30	ml.
B. Water (125°F., 52°C.)			
Metol	30 ounces	750	ml.
	39 grains	2.2	grams
Sodium sulphite, anhyd.	3 ounces 368 grains	96	grams
Hydroquinone	168 grains	8.8	grams
Sodium carbonate, anhyd.	1 ounce 400 grains	48	grams
Potassium bromide	90 grains	5	grams
Water to make	40 ounces	1000	ml.

Hydrazine dihydrochloride is also sold as Eastman Organic Chemical No. 1117. 6-nitrobenzimidazole nitrate is Kodak Anti-Fog No. 2; 36 grains (2.0 grams) of the solid are dissolved in 40 ounces (1000 ml.) of hot distilled water to make the 0.2% solution.

The chemicals are dissolved in the above order. Just before use a working solution is prepared by mixing 1 part of solution A with 32 parts of solution B (which is the ordinary Kodak D19 formula). The working solution does not keep.

The developer is used like a normal dish or tank developer.

The approximate time of development at 68°F. (20°C.) with intermittent agitation is about 16 minutes for normal films in Group B (see page 38).

The best useful speed increase is obtained by development to a fog density of 0.4, though fog densities of up to 0.6 can be tolerated. This will give rather dense and flat negatives which will need long printing times. They can, however, be reduced as described on page 344ff., to remove this fog. The best reducer for this is Farmer's reducer (No. 220 on page 342).

Exact development times can be found by cutting up a trial under-exposed negative into several strips, and developing these for a range of times from 10 to 20 minutes. The strip showing the best compromise of a low fog density with a satisfactory speed increase can then be taken as standard and its time of development as the standard time for that

material. It must, however, be remembered that even then much depends on how badly the negatives were under-exposed. With only slight under-exposure it is not necessary to develop to as high a fog density, nor will the gain in emulsion speed be as apparent.

#### DEVELOPMENT TO COMPLETION

We have seen that the time of development is of great practical importance (page 38) and has a real influence on the practical sensitivity of our material. To utilise fully the whole sensitivity of our material we must develop it "completely".

If we say "completely" we do not necessarily mean development to maximum gamma (page 35), i.e., development to finality. This would lead to very contrasty negatives giving poor photographic results. It is obviously not wise to over-develop but the development must be kept within such limits that a gamma value is reached which still gives an acceptable print. This is the reason why the British and American standard specifications for the measurement of film speed give a definite development time in a standard M.Q. developer. The speed figure of the product is based on such a procedure even if the material gives a higher speed figure at longer development.

The photographer might therefore, much to his surprise, find in practice that he can get higher speed by over-developing his film. In cases of emergency this can be useful and the result may be quite acceptable under certain conditions, especially if the original subject is flat.

As longer development leads to increased contrast it is advisable to use a soft working developer, for instance, the fine grain developers Nos. 80-93 or the high-definition developer Nos. 105-109. In some cases it may be more convenient instead to raise the temperature to about 77°F. (25°C.).

The gain in speed depends on the type of emulsion—some films are more suitable for this method than others. But in the most favourable circumstances the increase in speed is not likely to be more than two or three times. If speed tests are not carried out under controlled conditions results can easily be very misleading and this explains probably the exaggerated claims advanced from time to time.

# *Fixing*

## WHAT THE PROCESS IS AND HOW IT WORKS

When we expose and develop a plate or film, only about 25% of the silver bromide in the emulsion is used up in forming the negative image. The balance, which has not undergone any change in the developer, must be removed in the fixer if the negative is to be clear and permanent.

As a fixing agent hypo is used almost exclusively. To the chemist hypo is sodium thiosulphate, but the photographic world always calls it hypo. Other silver halide solvents are: alkali thiocyanates, cyanides, sodium sulphite, ammonia, thiourea, thiosinamine, concentrated solution of potassium iodide. Some of these fixing agents are used for special purposes.

Fixing is no simple process of solution like the dissolving of a lump of sugar in water; it involves a series of reactions in which the silver bromide is converted into a series of complex argentothiosulphates containing varying ratios of silver to thiosulphate (H. Baines 1929). The first reaction between a silver halide and hypo forms a rather insoluble and not stable compound. If at this stage the fixing process is stopped, the negative will not be permanent and will have a milky appearance. The intermediate compound reacts with more hypo to form finally very soluble complex compounds of sodium argentothiosulphate, which can be easily removed.

This short summary of the fixing process shows how necessary it is to allow sufficient time for proper fixation if we are to obtain permanent negatives. A useful rough rule is to allow at least double the time that is required for the clearing of all trace of milky appearance from the film. Only by so doing can one ensure that no deleterious residue is left behind which will affect the permanence of the negative.

## XLVIII.—FIXING BATHS

[illegible]

Two points emerge from the consideration of the nature of the fixing process, first that a sufficient excess of hypo must be present in the bath in order to form the easily soluble double salt, and also that it is not good policy to use too strong a bath. From what has been said it will be clear that the disappearance of the milky silver bromide from the film is not necessarily evidence that the bath is working normally. Unless the necessary excess of hypo is there the soluble double salt cannot be formed and cannot therefore be dissolved out.

It may also just be mentioned that economy in fixing baths does not pay with hypo being as cheap as it is.

#### RATE OF FIXATION

The clearing time or the practical rate of fixation is, according to C. E. K. Mees, affected mainly by the following factors:

- (1) *Nature of emulsion.* The clearing time varies with the silver halide content of the emulsion, the composition of the silver halides and, to quite a considerable degree, on the grain size.  
It is much shorter for fine-grain than for coarse-grain emulsions because of the much greater total area of the finer grains. It is also apparent that the clearing time will vary with the path of diffusion of the fixing solution in the emulsion and is thus longer for thick emulsion layers than for thin ones. Sheppard and Mees found that, rather unexpectedly, the hardness of the gelatine has practically no effect.
- (2) *Concentration of thiosulphate.* As one would expect, the fixing time decreases with increase of thiosulphate concentration, but only up to a certain maximum. The optimum concentration is between 30 and 40%.
- (3) *Nature of the thiosulphate compound.* The fact that ammonium thiosulphate is more rapid than the sodium compound has been known for a long time but it is only comparatively recently that fixing preparations containing ammonium thiosulphate have found wide application in practice. Such

preparations had gained a reputation for producing less stable images than plain hypo and only recently have investigations proved that that this is not the case. Another reason why the more rapid fixing action of ammonium thiosulphate was not made wider use of before is the fact that this fixing agent was not available in the stable pure form in which it is now produced. It was therefore the usual practice to produce ammonium thiosulphate in the solution itself by adding ammonium chloride to the hypo bath. Table XLIX shows that the clearing time can be considerably shortened and that the optimum is reached at a concentration of 20% hypo and 4% ammonium chloride. However, still better results can be obtained by using ammonium thiosulphate which has about 50% more rapid action than the mixture of hypo and ammonium chloride.

**XLIX.—EFFECT OF AMMONIUM-CHLORIDE ON CLEARING TIMES**  
(C. W. Piper)

Ammonium chloride %	Sodium thiosulphate (Clearing times in minutes)		
	10%	20%	40%
0	12	5	3
2	5	3	2
4	4	2	4
6	4½	2½	5
8	4	2½	6½
10	4½	3	8
12	5	3½	9
14	5½	3½	12
16	6	4	12½
18	6½	4½	14
20	7	4½	over 15'



**L.—CLEARING TIME IN SODIUM THIOSULPHATE**  
(C. E. K. Mees)

Sodium thiosulphate %	Time in Minutes		
	13°C. 55°F.	18°C. 65°F.	24°C. 75°F.
10	longer than 10	9½	7
15	8	7½	5
20	6	4½	4
30	4	3	3
40	3	2½	2½

- (4) *Temperature.* Higher temperature accelerates the fixing process as shown by Table L. The effect is more pronounced at lower concentrations of hypo than at higher ones. The best practical working temperature is between 65 and 75°F. (18 to 24°C.). Below this range the action may be too slow while above it the gelatine may become too soft.
- (5) *Agitation.* Agitation increases the rate of fixation by supplying fresh solution to the emulsion and removing reaction products from the emulsion surface. However, in practice the effect is not very pronounced because the differences between the specific gravities of the fresh solution and the reaction products leads to convection currents which "agitate" the solution to some degree.
- (6) *Exhaustion.* A number of changes take place in the composition of the fixing bath while it is used. Reaction products accumulate and the solution becomes also more and more diluted as a certain volume of water or developer is carried in by each film. The degree of exhaustion of the fixing bath must therefore be carefully watched.

**LI.—CLEARING TIME IN SODIUM AND AMMONIUM  
THIOSULPHATE (at 20°C.)**  
(C. E. K. Mees)

<i>Concentration</i>	<i>Sodium Thiosulphate Time in Minutes</i>	<i>Ammonium Thiosulphate Time in minutes</i>
10%	7	2
20%	5	1½
30%	3½	½
40%	3½	½
50%	—	1
60%	—	1½
70%	—	2½

**LIFE AND CAPACITY OF FIXING BATHS**

If permanent negatives are desired, it is very important that the fixing bath should not be overworked. It is impossible to control the condition of the fixing bath by mere visual examination. A fixing bath near exhaustion will still apparently clear the negative but the not easily soluble silver salts will remain in the film. It should, therefore, be a rule to discard the fixing bath when it takes twice as long to clear the film as it did when the bath was fresh. The exhaustion figures of Table LII should be taken as a safe maximum.

**LII.—CAPACITY OF A FIXING BATH**

<i>Size of Film</i>	<i>Number per 1 litre</i>
Sheets 8 × 10 in.	25
Roll film 120 or 620	25
Roll film 127	50
35 mm. film (36 expos.)	25
Sheets 6½ × 8½ in. or 18 × 24 cm.	40
Sheets 4½ × 6½ in. or 13 × 18 cm.	60
Sheets 4 × 5 in.	100
Sheets 3½ × 4½ in. or 9 × 12 cm.	150

All fixing solutions have good keeping properties. In an open tank they can be kept for at least one month; in a well stoppered bottle they will last for three months or longer.

A simple method to determine the degree of exhaustion is the use of indicator papers:

- (1) *Test for Silver.* As we already know, overworked fixing baths contain complex silver thiosulphate compounds which are retained by the film and cannot be completely removed by washing. The silver contents of used fixers of all types can easily be estimated with Agfa or similar "Silver Estimating Papers".

A piece of test paper is quickly dipped in the fixer, shaken to remove excess liquid and laid on a clean white card. After about 15 seconds the colour of the test paper is compared with the colour patches of the chart supplied with the test paper. The nearest match indicates the silver content in grams per litre. For normal work in dishes or small tanks 3.5 gm./litre is a safe maximum. In large tanks silver contents of 10 gm./litre or more are sometimes reached, but 7 gm./litre is best regarded as the limit.

The degree of exhaustion of the fixing bath can also be tested with a 5% solution of potassium iodide. Add about 2 drops of this solution to 10 ml. fixer in a test tube. If no cloudiness appears, the bath is still fit for use. If there is cloudy precipitate which, however disappears on shaking, the bath is becoming used up, but if a permanent precipitate (silver iodide) is formed, the bath is exhausted.

- (2) *Test for acidity.* The acidity can be checked with indicator paper. The pH of working strength fixer should be between 4.2-4.5. The use of litmus paper is not recommended, it is better to determine the pH with a "Narrow Range" Indicator paper such as B.D.H. 4055. If the pH is close to 5, more acid must be added to the fixer, either a 50% acetic acid solution or a further quantity of the acid hardener stock solution.

### LIII.—STOP BATHS

[illegible]

## RINSE AND STOP-BATHS

Developers and fixing baths do not agree with one another, hence it is necessary to remove as much as possible of the developer from the negative before it is placed in the fixing bath. If this is not done, developer in the fixing bath can affect its working, shorten its life and give rise to a number of troubles. (See page 406.) In certain cases development may even continue in the fixing bath.

Hence the rinse between developing and fixing is not so unimportant as some people think. It should be short but thorough, and preferably in running water, or at least in water that is frequently renewed. There is no point in rinsing the negative in a bath which contains nearly as much developer as the developer bath itself.

It is better and safer to use a stop bath instead or as an auxiliary to the rinse. This is a weak acid solution containing usually about 2% of glacial acetic acid. The same purpose is fulfilled by a 3-5% solution of potassium metabisulphite or sodium metabisulphite. Such a stop-bath interrupts the action of the developer more or less immediately while in a water rinse the development can still carry on often to quite an extent until the developer is completely washed out. It is, of course, essential that the stop-bath is really acid and if it is continuously used it may be necessary to test it with an indicator as suggested for the fixing solution (page 277). It is often desirable to stop and harden the film at the same time, and if the processing has to be carried out at raised temperature this is absolutely imperative. The simplest stop-hardening

### LIV.—STOP AND HARDENING BATHS

	178	179 SB3	180	181	182	183	184
	SBI	AN216	SB4		OP207	D2S	G357
Acetic acid (glacial)	17	—	—	—	—	6.5	—
Chrome alum	—	30	30	—	15	15	20
Sodium sulphate	—	—	60	—	—	—	30
Potassium metabisulphite	—	—	—	50	15	—	—
Water to	1000	1000	1000	1000	1000	1000	1000

bath is about a 3% solution of potassium or chrome alum. To this solution acetic acid can be added. If sodium sulphate is added as an anti-swelling agent, the temperature has still less effect.

A number of formulae for these various types of stop-bath are to be found in (Table LIV).

#### PLAIN OR NEUTRAL FIXING BATH

Fixing baths consisting only of a solution of hypo in water are suitable for the fixation of negatives, but they are used in practice only on very rare occasions. It is vital, then, that no developer is carried over to the fixing bath. As we have already seen, the speed of fixation rises with the content of hypo up to a certain point.

The useful limit lies at about 40% of hypo and in practice the most generally useful concentration is in the region of 25-30%.

#### ACID FIXING BATHS

The acid fixing bath is the most widely used in practice. It promptly neutralises any trace of alkali brought over from the developer and prevents stains and other troubles that might otherwise arise from this source. Developing agent transferred into the fixing bath would oxidise pretty rapidly in a neutral solution, discolouring the bath and ultimately causing stains in the film.

Acidification of the bath cannot simply be achieved by the addition of any acid as many of them would decompose hypo and set free sulphur. Sulphurous acid does not decompose thiosulphate but as this acid itself is not stable, its salts are used, such as potassium metabisulphite or sodium metabisulphite.

Certain weak organic acids like acetic acid can also be used, but only together with sodium sulphite to produce sulphurous acid in solution.

A number of such acid fixing baths are listed in Table XLVIII. In the usual type of acid fixing bath, bisulphites are used and ammonium chloride can be added to speed up the fixing process (see page 266). It is also possible to replace hypo by ammonium thiosulphate to produce an acid rapid

fixing bath. In making up fixing bath solutions the following points have to be observed.

It must be noted that hypo, when dissolving in water, produces a noticeable lowering of temperature. It is, therefore, advisable to use warm water to accelerate the process of solution. However, after hypo is dissolved the solution should regain approximately room temperature before the acid component is added.

It is also recommended practice to dissolve the acid ingredient separately in a small volume of water, especially when the mixture of sodium sulphite and acetic acid is applied.

#### HARDENING AND FIXING BATHS

The advantages of the hardening-fixing bath are not confined to working at higher temperatures, they materially reduce risk of injury to the gelatine layer of the film at any temperature.

The actual hardening agent is usually chrome alum or potassium alum. Of these two agents chrome alum exerts the greater hardening effect, but chrome alum baths have poorer keeping properties than those using potassium alum. Usually, potassium alum is therefore used.

All hardening and fixing baths must contain a definite proportion of acid. Otherwise, alkali from the developer might precipitate the hardening agent. Normally, acetic acid is used, of course, in the presence of sodium sulphite for the reasons stated above. It has been found that acetic acid may be supplemented, with advantage, by boric acid, which increases the hardening, lengthens the life of the bath, and notably inhibits the formation of a precipitate even under adverse conditions.

To make up a hardening-fixing bath the various ingredients should be dissolved in the order given in Table LV. In the case of hardening-fixing baths with chrome alum the preferred method is usually to make up two stock solutions A and B as shown in Table LVI. Solution B, containing the chrome alum, has better keeping properties than the mixed working solution. It is also often found convenient to make up the fixer containing potassium alum from a stock solution, as given in Table LVII. To make up the working solution the

## LV.—ACID HARDENING FIX BATHS

	185 F15 PIF	186 F6	187 F7	188 F10	189 AN204	190 G306	191 IF19	192 AG305	193 ATF5	194 ATF2
Sodium thiosulphate	240	240	360	330	240	200	300	200	—	—
Ammonium thiosulphate	—	—	—	—	—	—	—	—	200	112
Ammonium chloride	—	—	50	—	—	—	—	—	—	—
Sodium sulphite anhyd.	15	15	15	7.5	15	12.5	—	20	15	15
Potassium metabisulphite	—	—	—	—	12.5	—	2.5	—	—	—
Acetic acid 28%*	48	48	47	72	75	70	—	55	55	—
Boric acid	7.5	—	7.5	—	—	—	—	—	7.5	—
Borax	—	—	—	—	15	—	—	—	—	—
Kodalk	—	15	—	30	—	—	—	—	—	—
Potassium alum	15	15	15	22.5	15	15	—	10	15	—
Chrome alum	—	—	—	—	—	—	12.5	—	—	15
Special additions	—	—	—	—	—	—	—	—	—	Sulphuric acid 5%
Water to	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000

\*Glacial acetic acid 3 parts, water 8 parts



**LVI.—ACID HARDENING BATHS**  
(With Chrome Alum)\*

	195 F16 AN202	196 AG306	197 AG308
<i>Solution A</i>			
Sodium thiosulphate	960	280	340
Sodium sulphite anhyd.	60	25	17
Sulphuric acid conc.	—	1.5	—
Sodium metabisulphite	—	—	37.5
Water to	3000	500	500
<i>Solution B</i>			
Potassium chrome alum	60	15	30
Sulphuric acid conc.	8	—	—
Water to	1000	500	500
Working solution	Add B to A	Add B to A	Add B to A

\*Chrome alum is a very poor fixer-hardener in practice. Potassium alum is to be preferred (see Table LV).

**LVII.—ACID HARDENING STOCK SOLUTION**

	198 F5a	199 F6a	200	201 D2 FH
Sodium sulphite anhyd.	75	75	50	60
Acetic acid*	235	235	75	190
Boric acid cryst.	37.5	—	—	—
Sodium metaborate	—	75	—	—
Potassium alum	75	75	100	60
Water to	1000	1000	1000	1000
Working solution	1 part stock solution to four parts 30% hypo solution			

\*Glacial acetic acid 3 parts, water 8 parts.

acid hardening stock solution is simply diluted with a 30% solution of plain hypo.

#### RAPID FIXING BATHS

In all these fixing solutions ammonium thiosulphate can be used instead of the sodium compound or a mixture of hypo with ammonium chloride.

When fixation has to be completed in 20 seconds or less, sodium or ammonium thiosulphate is not suitable. Satisfactory fixing agents for this purpose are potassium cyanide or ammonium thiocyanate. As the former is highly poisonous, ammonium thiocyanate is usually used.

Ammonium thiocyanate has its quickest fixing action at a concentration of 40-50%. If fixing has to be carried out in a matter of a few seconds, the temperature of the solution can be taken up to about 50°C. (122°F.). As solutions of ammonium thiocyanate have a liquefying effect on gelatine, 5% formalin might have to be added, even if fixing is carried out at normal temperature, in case the emulsion is not sufficiently hardened. Fixing with ammonium thiocyanate is especially suitable for high speed processing materials having thin and highly hardened emulsion coatings.

Solutions of ammonium thiocyanate are also suitable when the fixing process has to be carried out at a very low temperature, as they do not freeze above -18°C. At -7°C. for instance, fixing takes only about 4 minutes, whereas it would take 1 hour in ordinary hypo.

Another formula for a rapid fixing bath of this type is the following:

#### 202.—RAPID THIOCYANATE FIXER

Potassium thiocyanate	100 grams
Potassium alum	50 grams
Water to make	1000 ml.
Dissolve and add	
Acetic acid	35 ml.

#### FIXING BATH MAINTENANCE AND REGENERATION

The composition of a fixing bath, like that of a developer, changes with use. As the bath is used, more and more of the alkaline developer is carried over and the acid in the fixing

solution becomes exhausted. If an acid hardener fixing bath becomes neutral or alkaline, sludge may form and deposit on the negatives in the form of scum, which is very difficult to remove once the negatives are dry. Not only does the acidity decrease as the bath is used, but the clearing action itself becomes slower, due to overall dilution of the fixer. In addition, by-products are formed which increase fixing time and can also have an effect on the permanence of the negatives. To maintain the efficiency of the fixing solution, the following measures have to be taken:—

### 1. *Control of Hypo-concentration*

The drop in hypo-concentration can be overcome simply by maintaining the specific gravity, which should be measured with a hydrometer. There are hydrometers available which are scaled directly in grams of hypo per litre.

### 2. *Check of Acidity*

The acidity can be simply checked by the use of an indicator, either in the form of indicator solution or indicator paper. For use with acid hardening fixing solutions containing potassium alum, Bromo-cresol green is recommended as an indicator. A sample of the fixing solution is taken in a test tube and a few drops of the indicator are added. If a bluish-green colour instead of a green colour is obtained, a 50% solution of acetic acid is added to the fixing solution in the tank until a further indicator test gives the correct green colour. A yellow-green colour indicates that the solution is too acid, which might lead to decomposition of the solution by sulphurisation. In this case, small quantities of a 10% solution of sodium hydroxide should be added until a green colour is obtained. For testing the acidity of non-hardening fixing solutions or those containing chrome alum, the indicator Bromo-cresol purple should be used. If the colour of the test is purple, it indicates that the fixing solution needs more acid until a yellowish-green colour is obtained with the indicator test.

### 3. *Exhaustion of Fixers*

The degree of exhaustion of fixers can easily be determined with Agfa Silver Estimating Papers (see page 269). For normal work in dishes and small tanks 3.5 grams per litre is a safe maximum. In large tanks silver contents of 10 grams per litre or more are sometimes reached, but 7 grams per litre is best regarded as the limit.

Print fixers should be discarded when silver contents reach 1.75 grams per litre. For maximum print stability, 1 gram per litre should not be exceeded.

Even if the fixing solution is regularly replenished, the bath must be renewed from time to time as the clearing time will eventually become excessive. This is due to the build-up in the bath of alkali halides which slow down the fixing action and cannot be removed from the fixing solution. With silver recovery, the adding of replenisher can be continued for a considerably longer time than normally. However, when the clearing time is doubled, the fixing bath should be discarded.

Fixing bath regeneration is more reliable when electrolytic methods of silver recovery are being used. Of the chemical methods, the sodium-hydrosulphite process is in this respect the best one.

## MONOBATHS

The combination of developing and fixing in one operation and in one and the same bath is an old problem in photography to which a satisfactory solution has only been found quite recently. The idea of such a monobath is rather appealing as it eliminates separate stop and fixing and even hardening solutions. Moreover it requires no precise timing of development and it decreases the effect of variations in agitation, temperature and other processing conditions.

In view of these advantages it may seem remarkable that combined development and fixing, first suggested in 1889, has taken such a long time to become practicable. The answer lies in the fact that, in spite of the efforts of a great number of investigators, monobath formulae had a number of serious shortcomings. As a matter of fact, most of them were considered as inherent characteristics of the method. It seemed to be impossible to avoid loss of speed, the gradation and maximum density was unsatisfactory and there was pronounced tendency to produce fog. Keeping and exhaustion properties tended to be poorer than with conventional developers of similar type.

These drawbacks were overcome as a result of more recent research work, helped by the fact that modern films

are basically more suitable for the method than those available hitherto. Formulae, especially those based on the use of Phenidone, have been devised which produce results that are practically identical with those obtainable by conventional processing. The problem consists of combining a developer which acts so quickly that the development is finished before the fixation starts. But even while fixing has already started, development is probably helped by a process of physical development.

Many monobath formulae are based on M.Q. with a high proportion of sodium hydroxide as accelerator, (see Table LVIII.

Another point to be considered is the concentration of the monobath developer. When the usual concentration of conventional developing solutions are mixed with the usual concentration of hypo baths to form a monobath, no satisfactory result is obtained. For acceptable results the developer concentration has to be increased on an average by 5 times. At the same time the pH has to be raised to pH 11-12 while the hypo content has to be reduced.

To increase the stability and exhaustion properties until they are equal to those of conventional developers, potassium alum is added in Formula 203. Such a developer keeps a pH of 11.5 throughout its useful life. This buffer also helps to prevent excessive swelling of the gelatine and reticulation. Monobaths can be of very quick action, processing the film in approximately 3 minutes at 75°F. Where rapid processing is of importance, a monobath can be used at this or even higher temperature.

A number of published monobath formulae are based on the use of Phenidone and it is claimed that this leads to higher speed contrast and maximum density (Formulae 204, 206-208). In place of alum Formula 204 contains formalin which is a still more effective hardener, especially in alkaline solution and in the presence of sulphite.

The gamma value of a monobath is fixed by its composition and cannot be varied by change in dilution, time or temperature of development. It is, however, possible to obtain a wide gamma range without loss of film speed by the simple method of varying the hypo content. With Formula 204, for instance, a gamma range of 0.65-1.05 is obtained by varying the hypo content between 150 and 250 grams per litre.

## LVIII.—MONOBATHS

	203 <i>H. S. Keelan</i> <sup>1</sup>	204 <i>M. Levy</i> <sup>2</sup>	205 <i>C. Orlando</i> <sup>3</sup>	206 <i>Kodak Research Lab.</i> <sup>4</sup>	207 <i>A. Sasai and N. Mii</i> <sup>5</sup>	208 <i>G. W. Crawley</i> <sup>6</sup>
Metol	—	—	12.9	—	—	—
Sodium sulphite anhyd.	50	60	70.9	50	40	50
Hydroquinone	15	30	25.7	12	15	12
Phenidone	10	0.8-5	—	4	2	1
Hypo	110	75-250	180	110	25	70-125
Potassium thiocyanate	—	—	—	—	90	—
Sodium hydroxide	18	25	25.7	4	—	10
Sodium carbonate	—	—	—	—	40	—
Potassium alum	18	—	—	—	—	—
Formaldehyde (38%)	—	10	—	—	—	—
Antifog	—	—	Benzotriazole 10 g	—	2-Mercapto Benzthiazole 0.1 g	—
Water to	1000	1000	1000	1000	1000	1000

<sup>1</sup> Phot. Sc. 5, 144 (1957) <sup>2</sup> Phot. Sc. Eng. 2, 136 (1958) <sup>3</sup> Phot. Sc. Eng. 2, 142 (1958) <sup>4</sup> Phot. Sc. Eng. 5, 198 (1961) <sup>5</sup> Phot. Sc. Eng. 8, 270 (1964) <sup>6</sup> Brit. J. Phot. Annual (1974).

Using the same expedient, monobath formulae can be adapted to various types of films. They are basically not as universal as conventional developers and it may be necessary to alter the ratio between speed of developing and fixing to fit different emulsions. The speed of development can usually be controlled by the alkali content (pH value) while the course of fixation can be influenced by the amount of hypo.

G. Haist has summarised the variations in monobath formulation and processing conditions which may be used to modify the results obtained:

*To increase contrast and emulsion speed*

- (1) Raise the pH.
- (2) Increase the concentration or activity of the developing agents.
- (3) Reduce the concentration of the fixing agent.
- (4) Raise the processing temperature.
- (5) For more contrast increase the concentration of hydroquinone and for more speed increase the concentration of Phenidone or metol.

*To reduce contrast or emulsion speed*

- (1) Lower the pH.
- (2) Increase the concentration or activity of the fixing agent.
- (3) Increase the salt content or viscosity.
- (4) Use more vigorous agitation.

Although monobath formulae of Table LVIII have all used hypo a recent development\* has been the use of  $\alpha$ -thioglycerol as the fixing agent. This monobath formula (209) uses antimony potassium tartrate as a stabilising agent and it has been claimed that high-speed film such as Kodak plus-X

**209.—ULTRA RAPID MONOBATH**

(pH 12.65 by addition of potassium hydroxide)

Potassium sulphite	20 grams
Antimony potassium tartrate**	40 grams
Phenidone	3 grams
Hydroquinone	60 grams
$\alpha$ -Thioglycerol	150 ml.
Water to	1,000 ml.

\*\*toxic substance

\*L. Corben, C. Bloom, D. Willoughby and A. Shepp, J. Phot. Sci., 14, 297 (1966).

Reversal SO-273 can be processed in 2.5 seconds at 120°F. (48°C.) to yield results comparable with those of the film normally processed in D-19 developer.

#### FIXING AT LOW TEMPERATURES

Fixation, like development (see page 229), is less rapid at lower temperatures and it is therefore advisable to employ a bath of high activity i.e. fixing solutions based on the use of ammonium thiosulphate (Formulae 193, 194). The optimum concentration of ammonium thiosulphate fixers varies with the temperature and it may in fact be better to dilute solutions when the temperature is lowered. At a working temperature of 20-40°F. (minus 6 to + 4°C.) the standard fixing solution should be diluted with 3 parts of water and at the very low temperature 1 part of ethylene glycol has to be added to event freezing.

Much more rapid fixing can be obtained by the use of a thiocyanate bath (Formulae 202). A concentration of 40% potassium thiocyanate has been found about optimum for temperatures ranging from 20-70°F. (minus 6 to 21°C.). At 20°F. for instance the bath will clear the developed film in 3-4 minutes, whereas an ammonium thiosulphate bath would take over 1 hour. Since the freezing point of this thiocyanate bath is about 0°F. (minus 18°C.) no anti-freeze has to be added when working within this range. Thiocyanate fixing bath has the tendency to soften gelatine and may cause difficulties in washing and drying. This may be largely overcome by adding about 5% formalin as a hardener and making the fixing solution slightly alkaline by the addition of sodium carbonate.

If washing under these conditions offers difficulties, there are no objections to adding ethylene glycol to the wash water as an anti-freeze. The film can for instance be washed in 4 successive baths of a 25% solution (by volume) of ethylene glycol, 10 minutes in each change.

At very low temperatures it may be necessary to accelerate drying by the use of alcohol (see page 296).

#### THE RECOVERY OF SILVER

Silver is a rather costly material and its recovery is, therefore, worthwhile when it occurs in appreciable quantities in fixing



baths. Usually, only about 25% of the silver in sensitive materials forms the developed image: the balance finds its way into the fixing solution. When large quantities of photographic materials are used, the amount of silver so accumulated is appreciable. On average, the following quantities of silver are recoverable:

#### LVIIIA.—SILVER RECOVERY

<i>Film Material</i>	<i>Potentially Recoverable Silver (grams/100 units processed)</i>
B. and W. Negative (1-120, 1-135/36)	10-16
Colour Negative (1-120, 1-135/36)	32-36
Colour Reversal (1-120, 1-135/36)	24-28
"Lith" film (20.3 × 25.4 cm)	10-17
X-ray, industrial (35 × 43 cm)	155-249
X-ray, medical (35 × 43 cm)	46-93

#### DETERMINING THE AMOUNT OF SILVER IN FIXING BATHS

The amount of silver which a fixing bath contains depends naturally on the extent to which the bath has been used. On average, a silver content of 2-3 parts per 1000 parts of fixing solution can be expected, but it may go as high as 1 part per 100.

In most cases, it is not necessary to calculate the probable silver content of the fixing bath; it is sufficient to recover it. If determination is required, the usual analytical methods can be used, but they are normally beyond the capacity of the darkroom staff.

Kodak have produced an "Argentometer" which is very simple to operate, but rather expensive to purchase. It measures a depth of colour of a colloidal solution of silver sulphide by means of a photocell and so determines the amount of silver in the bath. Ilford have supplied a simpler "Silver Estimator" based on a visual colour test. To estimate the silver concentration, a sample of the fixer is compared with the test solution through a comparator which, when adjusted, indicates the concentration of silver in the fixing bath in grams per litre.

The simplest means of determining the silver content of used photographic fixers is by the use of Agfa Silver Estimating Papers. A piece of test paper is dipped in the fixer, the

excess liquid removed and the paper laid on a clean white card. After 15 seconds, its colour is compared with that of the chart supplied with the estimating papers. One compares it with the nearest two adjacent colour patches and takes the nearest match. One can then read on the scale the silver content in grams per litre.

The following method uses a similar principle of colour comparison. It requires two solutions:

#### 210.—TEST SOLUTION FOR DETERMINING SILVER

1. Water	40 ounces	1000	ml.
Hypo cryst.	4 ounces	100	grams
Silver chloride	54 grains	2.6	grams
2. Citric acid	180 grains	9	grams
Sodium citrate	4 ounces	100	grams
Water to make	40 ounces	1000	ml.
3. Gelatine	80 grains	4	grams
Water	40 ounces	1000	ml.

Add a few drops of clove oil to solution No. 3 as preservative.

The gelatine is first swollen in cold water, then heated on the water bath with stirring until completely dissolved, and finally made up to the correct volume.

4. Sodium sulphide	$\frac{1}{2}$ ounce	12	grams
Sodium sulphite	$\frac{1}{4}$ ounce	6	grams
Water to	4 ounces	100	ml.

The standard solution for comparison is made by taking 4 ml. of solution 1 and adding 6 ml. of solution 2 followed by 10 ml. of solution 3. After diluting to nearly 100 ml., 2 ml. of solution 4 are added to the mixture which is then made up to exactly 100 ml. This provides a brown colloidal suspension of silver sulphide which keeps reasonably well in a stoppered vessel.

The standard solution gives a brown colouration resulting from 2 grams of silver per litre contained in solution 1 which can be compared with the colouration obtained by preparing a similar mixture using 4 ml. of the fixing bath in place of solution 1 and the same amounts of solutions 2, 3 and 4 and making up to 100 ml as before.

If now equal volumes of these two solutions contained in vessels of equal size (e.g. test tubes), that is, the standard and the one made from the fixing bath, are compared and are found to have identical shades of brown, they must contain the same quantity of silver, namely 2 grams per litre. If the

solution from the fixing bath is a deeper brown, it contains more silver.

Then take half the volume, add an equal volume of water and shake well and compare again. If now the colour is equal, then the fixing bath contains twice as much silver as the standard, namely 4 grams per litre.

One or two trials will be sufficient to determine fairly exactly how much silver the bath does contain.

Naturally such a method is not necessary for the single worker, but it is useful in the small business where it is useful to know how much silver baths contain and therefore the amount which can be recovered from them.

#### ELECTROLYTIC RECOVERY OF SILVER

Where large volumes of fixing bath have to be dealt with, this is the ideal method of silver recovery. It is clean-working and produces a very pure silver (92–99%). It also has the advantages of increased life and re-use of fixing baths, economy for large-scale operations and may be used for bleach-fix solutions. However, mention should be made of some of the disadvantages of this method of silver recovery. The equipment is relatively expensive to buy although some suppliers operate rental schemes. To ensure efficient operation the process of recovery must be accurately monitored and controlled and time is needed to strip the silver from the cathode. The units occupy space which may be a problem in a crowded processing laboratory.

All electrolytic silver recovery units operate on the same principle of two electrodes (an anode and a cathode) being immersed in a silver-containing fixer through which a direct current is passed which causes silver to be deposited on the cathode. Early attempts at silver recovery by this method led to the formation of silver sulphide on and around the cathode due to the electrolytic decomposition of the thiosulphate ion to sulphide ion, which then reacted with silver ions to form silver sulphide. This problem has been overcome by the use of efficient agitation either by a rotating stainless steel cathode or by causing the fixer solution to move rapidly past stationary electrodes. These methods ensure that there is a sufficient supply of silver ions near the cathode, because silver is in the form of a negatively charged silver-thiosulphate complex which, if left

to its own devices, would migrate away from the cathode where the plating out of metallic silver takes place. The current density (current/unit area of cathode) requires careful control. If too high a current density is used for a fixer solution containing little silver, sulphiding occurs. If too low a current density is used, silver recovery is very slow. Some of the simpler units, however, do use low current densities but employ a large cathode area and have the advantage that no agitation is required. Generally, high current density units operate at around 1 amp/square foot for each gram of silver per litre and the minimum silver content of the fixer to be electrolysed should not be less than 1 gram per litre. Low current density units which operate at current densities less than 0.1 amp per square foot can recover silver from fixing solutions containing less than 0.1 gram per litre, although it is necessary to circulate the solution past a bank of electrodes of large surface area in order to increase the rate of recovery.

For the practice of silver recovery by this method it is necessary to control the current density carefully and to select a unit appropriate to the rate of fixer usage and concentration of silver in the fixer. Batch-type units may be operated at high current densities at the start of silver recovery when the silver content is high, but as recovery proceeds the current must be reduced or sulphiding will occur. Many units of the recirculatory type continuously keep the concentration of silver in the fixer to below 0.5 grams per litre with the result that any fixer carried with the film to the wash results in the loss of very little silver.

Some units operate on the overflow from fixing tanks and the de-silvered fixer is discarded. This method requires little labour in maintaining the activity of the fixing bath but the process of recovery must be checked. In those systems which re-circulate de-silvered fixer it is necessary to carry out proper chemical control of the recovery process. For example, during the electrolysis both thiosulphate and sulphite are converted to other products at the anode, so after recovery the fixer must be replenished with these chemicals to maintain its activity. For fixers containing 1–5 grams per litre the sulphite concentration should be maintained at approximately 8–10 grams per litre during the recovery process in order to inhibit the sulphiding reaction. Also the pH value should be maintained below 5 for efficient recovery. In some development processes alkaline

developer is carried over into the fixer and acetic acid is usually added to maintain the pH, whereas in some colour processes acidic bleaches are carried over and dilute sodium hydroxide should then be added.

Finally a small amount of gelatin or its degraded products cause the silver to be deposited evenly and smoothly on the cathode; normally sufficient dissolves from the films being processed.

#### PRECIPITATION OF SILVER BY OTHER METALS

Many metallic powders will precipitate silver from its solutions; the best results so far having been obtained by using zinc dust. It requires 3 parts of zinc dust to precipitate 1 part of silver; hence it is important to have some idea of the amount of silver present so as not to waste zinc.

The silver is precipitated in the form of a black mud which contains about 50% metallic silver. Under no circumstances should the precipitation be carried out in the vessel used as a fixing bath. The best way is to accumulate sufficient spent fixing bath liquor and precipitate a large volume at a time. A simple test to determine if the silver is completely precipitated consists in placing or hanging in the bath a small freshly-cleaned strip of copper or brass. If after a time the strip shows any trace of a white deposit of silver the precipitation has been incomplete.

When all the silver is thrown down it is allowed to settle, the supernatant liquor syphoned or poured off and the residue collected and dried.

A more recent adaption of this principle is by the use of steel wool.\* Theoretically one part by weight of iron (steel wool) should displace approximately four parts by weight of silver from used fixer solutions, but in practice only two to two and one half parts by weight are displaced.

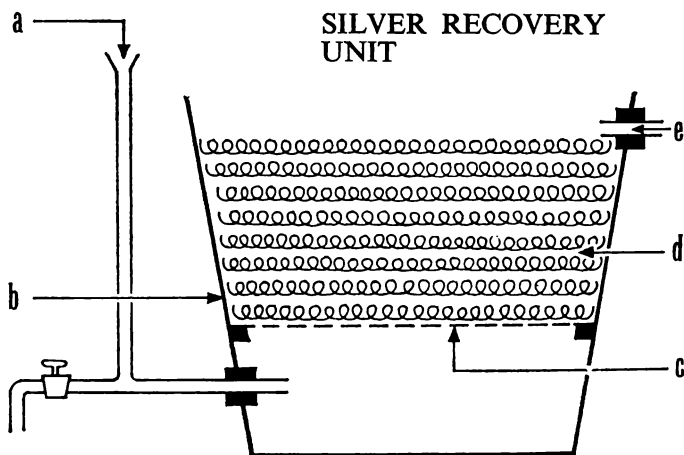
In this method used fixer solution is slowly passed upwards through a column of steel wool where iron passes into the solution and displaces the silver which is then held in the steel wool. Only exhausted fixer can be employed in this method; the effluent from the column cannot be used as a fixer because it is contaminated with iron.

The apparatus required is extremely simple and is illustrated

\*May & Baker, Dagenham, Essex. Leaflet "Silver Recovery from Amfix, Perfix and hyper Amfix High Speed Fixers, Use of Steel Wool".

in the diagram on page 288. It may be connected to the outlet of an automatic processor. The size of the vessel is limited by the rate of fixer usage, May & Baker recommend that fixer should pass through the apparatus in twenty-four hours to allow sufficient time for the exchange to take place. Thus if fixer is used at the rate of twelve gallons per day the vessel should be of twelve gallons capacity and the rate of flow should be one half gallon per hour. If less fixer than this is used per day it may be collected in a header tank until twelve gallons have been collected, or a smaller vessel could be used.

The exhaustion of the steel wool is readily determined by measuring the (high) silver content of the effluent or more simply by the visual appearance of grey flecks of silver in the upper layers of the steel wool. When this point has been reached the steel wool is removed from the apparatus and left to dry before sending to the refiners. The apparatus is then re-charged with steel wool and silver recovery may once again be started. This principle is also used in many commercially available silver recovery cartridge assemblies which can be



A typical steel wool silver recovery unit consisting of a tank of wood or plastic (b). Used fixer is run into the vessel (b) through (a) and passes upwards through the steel wool (d) supported on a perforated platform of wooden slats for example (c). Finally the fixer from which the silver has been removed, is run to waste via the exit tube (e) or into a second recovery vessel for more efficient removal of silver.

## PRECIPITATION OF THE SILVER BY SULPHIDE

This is the oldest and the cheapest method of recovering silver. It is obtained as a silver sulphide mud containing from 40-70 % of silver.

Sodium sulphide is usually used, although the potassium salt, liver of sulphur can be used but is more expensive. The great disadvantage of the method is the evolution of hydrogen sulphide gas which occurs. On this account the operation must always be carried out in the open air and as far away from the dark-room as possible, as sulphuretted hydrogen is fatal to sensitive photographic materials. The amount of hydrogen sulphide produced can be greatly reduced by neutralising the fixing bath with soda before the sodium sulphide is added. The bath can be tested with litmus paper to make sure that it is alkaline. In general, about one ounce of a 20 % solution of sodium sulphide is required for each 10 ounces of bath.

When the precipitate has settled the overlying solution is tested with a few drops of sodium sulphide solution. If no brown cloudiness is produced precipitation is complete; if not, then more sodium sulphide must be added. The residue is treated in the same way as if it had been precipitated by metal powder.

## PRECIPITATION WITH SODIUM HYDROSULPHITE

A somewhat expensive method, but one producing a clean and pure silver. Each part of silver in the bath requires 3 parts of hydrosulphite. ( $\text{Na}_2\text{S}_2\text{O}_4$ .) Precipitation is facilitated by warming the bath to about 120°F.

The required quantity of hydrosulphite is added, along with five times that quantity of anhydrous sodium carbonate.

## REGENERATION OF THE FIXING BATH

Many attempts have been made to find methods of precipitating the silver in such a way that the fixing bath would be regenerated and so could be used again. The only fool-proof method which allows of this is electrolysis, for all the other methods result in the accumulation of much unwanted material in the bath and in most cases result in the decomposition of some or all of the hypo.

# *Washing and Drying*

Fixation of a negative is always followed by a thorough washing, for in addition to correct fixing the permanence and good keeping properties of the negative are entirely dependent on the efficiency and completeness of the final wash which must remove every trace of fixing bath and all other soluble salts from the film.

## TECHNIQUE OF WASHING

Washing must never be attempted in a perfunctory manner. Its purpose will not be fulfilled unless the water is frequently replaced by a fresh supply, or else the washing is carried out in a stream of running water.

To attempt washing in a dish, or the arrangement shown on page 129, No. 1, is to risk failure because here the water is not efficiently renewed. A distinct improvement is to lead the water by means of a rubber tube so that it enters at the bottom of the dish. In this way the incoming stream of water catches up and mixes with the hypo solution dissolved out of the film and so removes it. Many of the washers on the market are provided with a syphon which empties them from the bottom of the washer, and so provides a practical solution to the problem.

The time required for washing naturally depends in some measure on the quantity of water available and the number of the negatives. With a good supply of running water 30 minutes should suffice, but if there are many negatives being washed this time may be increased to 40 minutes.

If running water is not available, then the water in which the negatives are washing must be changed at intervals of not more than 5 minutes, and 5-6 such changes are essential.

As to the quantity of water to use, use as large a volume



as possible but not less than about 8 ounces for each negative  $2\frac{1}{4} \times 2\frac{1}{4}$  ins. or *pro rata*. (200 ml. per square decimetre of surface.)

#### WASHING IN SEA WATER

The use of sea water for washing photographic materials is practical only when a final wash of about five minutes in fresh water is used. This final wash removes, as tests of the Kodak Research Laboratories have shown, the residual salts from the material and thus prevents rapid fading of the image caused by these salts in the presence of hypo, and absorption of moisture by the hygroscopic sea salts.

The removal of hypo is greatly accelerated during washing in sea water as compared with fresh water. As a result, it is recommended that films and prints be washed in sea water for about one-half of the usually recommended times, and finally for about 5 minutes in fresh water.

An increase of 20 to 40 degrees in the temperature of sea water increases the rate of washing by 25 to 50 %, but washing at as low a temperature as 50°F. (10°C.) removes the hypo more rapidly than at 70°F. (21°C.) in fresh water. The total time involved in washing in sea water followed by fresh water is therefore less than required in fresh water alone.

#### CONTROL OF WASHING

The occasion may arise when it is necessary to test the efficiency of washing or to discover how long it takes. It must be remembered that washing must remove not only every trace of hypo but also any soluble silver salts in the film. Two tests serve to find out whether washing has been complete. The first is for the hypo.

##### 211.—HYPO TEST SOLUTION

Distilled water	750 ml.
Acetic acid, glacial	35 ml.
Silver nitrate	7.5 grams
Distilled water to make	1000 ml.

The solution should not be allowed to come into contact with photographic materials, hands or clothing. It will stain

them black. The solution should be stored in a dark bottle away from light.

To make the test, cut a portion from the film and immerse it in the solution for 3 minutes. Any staining on the film indicates the presence of hypo, and the entire film should be re-washed and tested again until little or no staining occurs.

To test for residual silver the following solution is used.

#### **212.—SILVER TEST SOLUTION**

**2% solution of sodium sulphide**

This test should not be carried out in the darkroom. To make the test first remove excess moisture from the film by squeegeeing, and then place a drop of the silver test solution on the edge of the film. After about 3 minutes remove the solution with clean white blotting paper. A discoloration, other than a just noticeable cream stain, indicates the presence of residual silver compounds.

Another test is to take a strip of unexposed and undeveloped film and fix and wash it simultaneously with other material. When washing is considered complete, this strip is immersed in the above silver test solution. Any trace of silver salts in the film will give rise to a brown coloration.

This test is also useful in that it can indicate that the fixing bath is exhausted, and that insoluble silver salts are remaining in the film. In this case the strip of fixed and washed film is divided into two. One part is tested when washing should be complete. If discoloration occurs the washing is continued for another 15 minutes and the second strip is tested. If this still shows the discoloration then the fixing bath is not working properly and must be replaced by a fresh one, and the whole of the material washing must be re-fixed and washed again.

#### **SHORTENING WASHING BY CHEMICAL MEANS**

The fact that washing is normally a long operation has led many people to attempt to shorten it by chemical means. A number of substances have been used, all of which are oxidising substances which destroy or decompose hypo.

It must be admitted that the value of such methods is very doubtful. Unless they are used in very dilute solution, there is real danger of their attacking the image. There is also

the possibility that the products of the reaction will remain in the film and have a bad influence on its keeping properties. Hence even when they are used a short wash must follow.

A better method is to use:

#### 213.—HYPO REMOVER

5-10% solution of sodium carbonate or bicarbonate

in which the negative is bathed for 5 minutes. A short wash will then remove every trace of hypo.

A hypo-eliminator, recommended by J. L. Crabtree, C. T. Eaton and L. E. Muehler consists of two volatile chemicals, hydrogen peroxide and ammonia. This combination oxidises hypo to sulphate which is inert and excess eliminator, being volatile, evaporates. The new eliminator is intended for use with paper positives or negatives. It is difficult, if not impossible, to remove the last traces of hypo from paper and, as a result, the sulphur in the residual hypo sooner or later attacks any silver image forming a yellowish-brown silver sulphide.

#### 214.—HYPO ELIMINATOR FOR PAPER MATERIALS

Water	20 ounces	500 ml.
Hydrogen peroxide 3% solution	5 ounces	125 ml.
Ammonia 3% solution	4 ounces	100 ml.
Water to make	40 ounces	1000 ml.

To make 3% ammonia dilute one part of .880 ammonia with 9 parts of water.

Paper prints or negatives should be given as thorough a wash as possible, about 30 minutes at 65-70°F. (18-21°C.) in running water. At lower temperatures the washing time should be increased and for double weight prints or X-ray paper negatives the time should be doubled. Then immerse each print in the hypo-eliminator for about 6 minutes at 70°F., 21°C.) and finally wash for 10 minutes. About 50 prints 10 × 8 or equivalent can be treated in one gallon of the solution.

With negatives or transparencies on glass or film hypo can usually be removed completely by water alone without the use of a hypo eliminator. If the washing process has to be speeded up then a supplementary alkaline bath can be

used. The negatives, etc., can be washed in running water for ten minutes and then treated in the following bath.

#### 215.—HYPO ELIMINATOR FOR NEGATIVES

Ammonia .880	4 ounces	100 ml.
Water to make	40 ounces	1000 ml.

The negatives are bathed in this solution for 3 minutes and then washed for 2-3 minutes.

This formula is preferable to No. 213 as being volatile there is no solid residue left in the gelatine film of the negative.

#### DRYING

When washed, negatives should be dried in a dust-free place. Film can be hung free with a fairly heavy clip below to prevent air currents blowing it about too freely. Plates should be in a drying rack.

Before being put to dry, both sides of negatives, whether plates or films, should be gently but firmly wiped with a piece of viscose sponge or similar material, to remove all superfluous water.

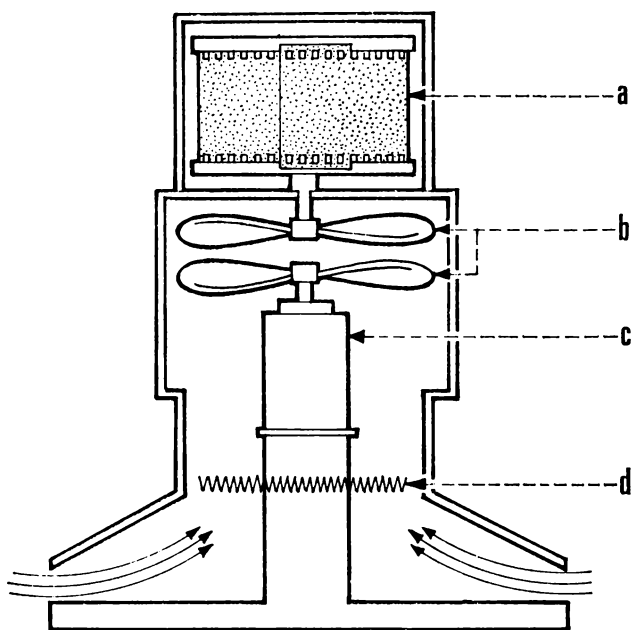
Not only does this accelerate the drying, but it removes any spots or flecks of gelatine which may have settled on the film, and it removes the possibility of small areas of irregular density due to drops of water on the film.

Drying can be accelerated by using warm air propelled by a fan. The temperature should not exceed 85-88°F. (30°C.), otherwise melting of the gelatine may occur. In the larger drying cupboards used in the photographic business the heating unit is part of the whole installation (see page 297).

Small blower dryers are available that dry the film without removing it from the spiral. In these dryers (see page 295) air is blown upwards through the film on the reel and drying may be accelerated by warming the air. It is claimed that in this method there is less risk of dust settling on the film than when the film is hung up to dry in an ordinary room.

Where very rapid drying is necessary an alcohol bath may be used.

## FILM DRYER



Film dryer: (a) the film on its spiral, (b) fan blades, (c) electric motor, and (d) heating element.

#### **216.—BATH FOR RAPID DRYING**

Dilute the spirit with 10-20% water

Dilution of the spirit is necessary to prevent attack on the celluloid of the film. The bathing should last 3-4 minutes and the film can then be rapidly dried in a current of air. With methylated spirits there usually occurs a more or less milky turbidity in the film, but this does not usually interfere with the printing from it.

Another method of quick drying depends on the use of a concentrated solution of a salt:

#### **217.—ALTERNATIVE BATH FOR RAPID DRYING**

Saturated solution of potassium carbonate

In this the film is immersed for a minute and then wiped dry with chamois leather.

#### **218.—ALTERNATIVE BATH FOR RAPID DRYING**

Saturated solution of magnesium sulphate (Epsom salts)

may be used for a like purpose; in this case the film is given half a minute in the salt solution, then squeegeed free from excess solution, given a spirit bath for a second or two and then dried in a few seconds in the stream of air from a fan.

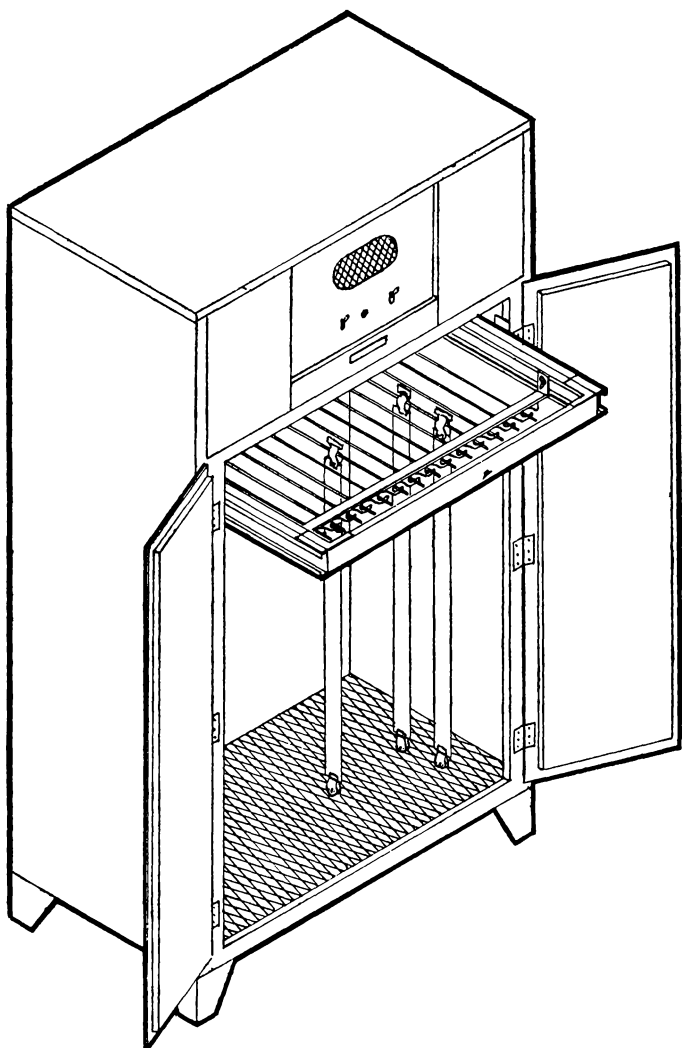
These methods of very rapid drying are used in press work where often every second is of importance. Negatives dried by such means are usually used to produce enlargements. If they are to be preserved they should receive a thorough washing as soon as they have provided the necessary enlargements, otherwise the presence of salts in the film will lead to damage and disintegration.

#### **STABILIZATION**

In cases where it is important to save time and the permanence of the print is of secondary importance, the developed image can be treated with a stabilizing agent without washing afterwards. The purpose of this stabilizing agent is to make the undeveloped silver halide substantially light fast and give it a certain amount of stability.

According to W. L. Brice, H. D. Russell and E. C. Yackel the stabilizing agent must be a compound which does not

## DRYING CUPBOARD



Heated air is blown down through the cabinet and out through the gridded floor. A filter is fitted in the air inlet to the cabinet. Interlocking double doors give easy access to the interior.

react with metallic silver but forms a light-inert silver compound by reaction with the undeveloped silver halide. The resulting silver compound should be light-coloured or transparent, so that it does not interfere with the viewing or printing of the final image.

Stabilizing agents which may be employed are organic compounds containing double-bonded sulphur or an SH linkage, and include alkali metal and ammonium thiosulphates and thiocyanates, thioureas, and thioglycollic acid. Compounds containing a quaternary nitrogen atom, such as  $\alpha$ -picolinium- $\beta$ -phenylethobromide, may also be employed. The agents are generally used in lower concentration than they would be in normal fixing procedures, where the emulsion is washed after fixing.

Specific stabilizing agents which may be used, together with the useful concentrations (by weight) in aqueous solutions, are as follows:

Potassium thiocyanate	10%
Ammonium thiocyanate	5%
Sodium thiosulphate (crystalline)	10%
Potassium thiosulphate	10%
Ammonium thiosulphate	10%
Thiourea	2%
Ethylene thiourea	2%
Propylene thiourea	2%
Thioglycollic acid (Na salt)	10%
$\alpha$ -picolinium- $\beta$ -phenylethobromide	10%

Other stabilizing compounds which may be used in various concentrations are the following:

Thiobarbituric acid  
 Ammonium dithiocarbamate  
 2-Mercapto-4-methyl-5-nitro-thiazole  
 2 Mercapto-4-methyl-thiazole  
 Dithio biurea  
 4-Aminomethyl-2-mercapto imidazole  
 5-Amino-2-mercapto-1, 3, 4-thiodiazole  
 2-Mercapto-5-amino-benzimidazole  
 6-Amino-2-thio-4-hydroxy-pyrimidine  
 Dithio oxamide



Thio trimethyl acetamide  
Cysteine hydrochloride  
Thioacetamide  
Thiopropionamide  
Thioglycollic hydrazide

#### FORMULATION OF STABILIZERS

The concentrations given above are based on a treatment or immersion time of about 30 seconds. Lower concentrations might be used with longer application or immersion times. The upper limit of concentration is defined by the solubility of the reagent and the general tendency toward crystallisation in the photographic material when very high concentrations are used.

The time of treatment will vary with the nature of the film (that is, the grain size and chemical composition), the temperature of treatment and the manner of application of the stabilizing solution. The time necessary for the application of a given stabilizing solution may be readily judged by inspection of the emulsion layer. It is necessary that the silver halide shall have disappeared from the emulsion and the disappearance of the halide, which indicates the formation of a complex with the stabilising compound, may be determined by inspection of the emulsion layer. When the silver halide has just disappeared from the emulsion, stabilization is complete.

The thiosulphates and thioureas are used in acid solution, the thioglycollic acid in alkaline solution, and the thiocyanates in either acid or alkaline solution.

According to D. J. Norman and P. G. Lungley,\* experience has shown that prints stabilized with ammonium thiocyanate are permanent in an atmosphere of low humidity, but that under conditions of high humidity the silver image is attacked and may eventually become bleached out. It is therefore desirable to apply the minimum quantity of ammonium thiocyanate to the print.

#### IMPROVEMENT OF STABILITY

The stability can be further improved by using a solution containing both ammonium thiocyanate and ammonium

\*British Patent No. 876,497 (1961).

chloride. In general, the best results are obtained when the said stabilizing solution is prepared by saturating ammonium thiocyanate solution with ammonium chloride at room temperature. The concentration of ammonium chloride in this saturated solution will vary with the concentration of ammonium thiocyanate. A very satisfactory stabilizing solution for use in the case when the stabilizing solution is applied in the form of a film to the developed emulsion layer contains 180 grams per litre of ammonium thiocyanate and 180 grams per litre of ammonium chloride.

John William Glassett and Frank Shirley Sutton\* have disclosed a photographic process utilising an ascorbic acid or a salt for the purpose of reducing the adverse effect of excessive humidity on the developed image. The ascorbic acid or salt is added to a stabilizing solution containing ammonium thiocyanate and the ammonium chloride. Suitable ascorbic acids or salts which may be included in this stabilising solution are l-ascorbic acid (commonly known as "Ascorbic acid") iso-ascorbic acid (also known as "Erythorbic acid" or "D-araboascorbic acid"), or a salt of either of these acids. If desired, a mixture of l-ascorbic acid and iso-ascorbic acid may be used in the said stabilising solution.

The invention is illustrated by the following example: A silver chloride emulsion containing hydroquinone is developed by the application of 5% caustic soda solution. The excess alkali is removed by a squeegee, and immediately afterwards there is applied to the material, by means of a roller, a film of stabilising solution made up according to the following formula:

#### 219.—STABILIZING SOLUTION

Ammonium thiocyanate	180 grams
Ammonium chloride	180 grams
Ascorbic acid	20 grams
Water to	1000 ml.
Ammonia (S.G. 0.910)	6 ml.

The quantity of ammonia is sufficient to raise the pH of the stabiliser to about 4.5. The excess stabilising solution is afterwards removed from the surface of the material.

\*British Patent No. 875,878 (1961).

## *Rapid Access Processes*

Rapid access processing can be defined as a technique that produces a usable picture in much less time than is possible by conventional processing methods, usually in the order of a few seconds and in some cases even in fractions of a second. In contrast to normal processing, in rapid access processing the solutions are applied by special applicators.

### CELL AND CHAMBER PROCESSORS

Cell and chamber processors permit the contact of small amounts of processing liquids with the emulsion and the film. A narrow space is provided between the film emulsion and the processing device. In a processor of this type, designed by K. H. Lohse and M. B. Skolnik\* the film is first located over a sealing frame, and then held tightly against the seal by means of a pressure plate. Through the centre bore of the processing platen, metered volumes of processing solutions are brought into the capillary chamber. The liquid could freely overflow the platen but is held within the chamber by capillary forces.

The chamber dimensions are critical and must be optimised. Good processing results have been obtained using a chamber depth from 0.010 to 0.030 in. A nearly square frame of 1.16 by 1.06 in. is preferred; however, equal success has been attained with a more rectangular frame of 1.16 by 0.92 in.

The volume of processing liquid required to fill the chamber ranges from 0.3 to 0.5 ml., depending on the frame size. The figures given apply to the processing of a 35 mm. double frame. Since the processing solutions contact

\*Phot. Sci. and Eng. 5: 149 (1961).

the emulsion side of the film only, this process is well suited to ultra rapid processing.

After development is complete, the fixing solution is introduced into the capillary chamber through the centre bore. This pushes the developer into the overflow and then into the waste container. Any intermixture of the two liquids is counteracted by the strength of the fixing solution, which not only rapidly stops the development but also completes the fixation of the image in the presence of traces of the developing solution. A wash solution follows the fixing solution after fixation is completed. Four to eight times the chamber volume will yield sufficient washing. The processing cycle is completed by drying the emulsion with a hot, high-velocity airstream which enters the chamber from the side and is directed evenly over the film surface. The drying air, which escapes through the waste spacing into the vented waste container, cleans and dries the chamber as well as the film.

The emulsion of the film and the desired image characteristics determine the selection of processing solutions. The capillary chamber process permits great flexibility in this area, for any wet process can be used with this technique. Monobath processing yields acceptable results, although in certain applications, such as the one mentioned above where image requirements of high contrast combined with low fog level are desired, better results are attainable if development and fixation are separated.

While this processing technique is not limited to the use of certain types of emulsions, it has been noted that for ultra rapid processing those emulsions especially designed by the manufacturers for rapid processing applications give superior results.

*Processing cycle:* The capability of the capillary chamber process may be illustrated by the following typical processing cycle:

Development for 1.5 seconds, followed by

Fixation for 0.5 second, and

Washing for 1 second.

The film is then dried in 2 seconds, giving a total processing time of only 5 seconds.

The processing platen, which is part of the heater block contains heating elements and a temperature sensing probe. The preselected processing temperature is automatically controlled and is maintained within  $\pm 0.5^{\circ}\text{F}$ . The processing temperature can be set for any point from ambient to  $130^{\circ}\text{F}$ . Although high-temperature processing is not necessarily needed for ultra rapid processing, it has been found that, at varying ambient conditions, elevated processing temperatures can be maintained more easily.

Using a developing chamber with a cavity of approximately 0.005", C. Orlando\* has developed a method for the production of photographic data recording 1/5 second after exposure. The 35 mm. film used for taking the photograph makes a seal with the lips of the chamber during the processing operation. The developing solution, which is preheated to  $170^{\circ}\text{F}$ ., is sprayed on the film through a narrow slit located on the upper section of the chamber. The developer is withdrawn from a slit on the lower end by means of a vacuum produced by a self-contained pump. After development, which normally takes 0.6 second, the film is kept in this chamber and hot air saturated with acetic acid vapour is drawn through the liquid ports. The hot air dries the film and the acetic acid vapour neutralises the alkaline developing solution and stabilises the image. The stabilisation, however, is not complete and a yellow light is used for projection to prevent fading of the image. The drying and stabilising operation takes a little less than 1 second so that the image can be projected approximately 1.5 seconds after exposure.

For processing, the monobath (Formula 205) gave excellent photographic results at  $140^{\circ}\text{F}$ . and 1.3 second processing time. However, a serious difficulty was encountered which made the technique impractical. The monobath solution forms a silver compound which precipitates and adheres to the surface of the developing chamber and its liquid ports. Since these ports are very narrow—approximately 0.005 in. wide—any foreign deposition causes restriction to the liquid flow sufficient to make the equipment inoperative after a very short time. A two-bath system is more reliable but involves the use of two chambers, one to develop the film, the other to clear it. For development, Formula

\*Phot. Sci. & Eng. 2: 142/147 (1958)

127 is used at 185°F., and for fixing a 50% hypo solution at 205°F. Each step requires only 0.2 second.

#### VISCOUS LAYER APPLICATORS

In selecting a processing method for a machine to be designed for both rapid and simplified processing, the viscous technique has found commercial application on a large scale.

P. A. Hermle and H. D. Lowry\* have described a machine which processes 16 mm. black and white positive films at 36 ft./min., with a dry-to-dry time of one minute. The developer and fixing solutions are each coated on the emulsion surface as a viscous layer in an atmosphere saturated with water vapour at 125°F. The viscous processing solutions are packaged in one-gallon disposable collapsible polyethylene bags which can be changed without interrupting the processing operation.

The film enters the processing chamber from the feed chamber and passes round the coating roller. At this point viscous developer is applied to the emulsion surface by the coating hopper in a layer approximately 0.008 in. thick. The reaction loop of the developer is adjustable by raising or lowering the roller to provide developing times of 2½ to 7 seconds. By this means a specified contrast may be selected.

The developer coating is removed by a high-velocity water spray jet. The surface water on the film is removed by a Venturi-type air squeegee. The film then passes round a second coating roller where the viscous fix is applied by another coating hopper. Two helical loops are required for the fixing time of 12 seconds.

The coating of viscous fix is removed by a second spray jet at the bottom of the second loop. The film then passes beneath a partition and into the wash compartment. Three helical loops are formed in the wash stage with the film emulsion toward three spray nozzles having a hollow, conical spray pattern. The bottom rollers are adjustable to give washing times of 13 to 17 seconds. After passing through a second Venturi squeegee, the film goes into the impingement air dryer. The bottom roller assembly for the three loops in the dryer is adjustable to give times of 15 to 21 seconds. In

\*S.M.P.T.E. 70, 875-877 (1961).

summary, the processing sequence includes: viscous developer, spray cut-off, air squeegee, viscous fix, spray cut-off, wash, air squeegee, and dry.

The hoppers of the coating mechanism are made of two wedge-shaped stainless steel elements separated by a U-shaped plastic shim 0.008 in. thick. With the two halves in place, the shim forms a channel as wide as the film and 0.008 in. thick. The solution in flowing through this channel forms a smooth ribbon, which is applied to the emulsion. Both coating hoppers are hinged to permit the passing of splices.

#### POROUS PLATE AND ROLLER APPLICATORS

Rapid access processes based on the application of thin layers of solution to the emulsion surface by means of porous rollers or plates provide another technique.

A porous applicator processor, was described by R. P. Mason.\* The figure on page 310 illustrates its main features. A  $\frac{1}{8}$  in. thick porous plate, made from sintered stainless steel granules, is cut to the width of the exposed area on the film and to a length generally determined by the required film rate. It has been found desirable to limit the processing head to approximately 1 in. in length, and build up as many 1 in. modules as required for a particular length. In this case, a single head was utilised for each of the two processing solutions. The stainless steel plates are fastened to a manifold block which contains a feed pipe and a cavity containing a Dacron wick material. This aids in dispersing the solution flow uniformly through the porous material.

A pump rate is maintained which slightly exceeds the rate of solution carry-off, thereby forcing the meniscus to bulge slightly on all four free boundaries. The excess solution flows down the edge of the porous shoe from the boundaries of the meniscus, and is collected in a moat around the shoe. From there, it is drained by gravity or pumped into the waste tank. By means of cartridge heaters, the thermostatically controlled manifold block is heated to the temperature desired in the process. The solution flow rate is slow enough to permit the solutions to reach the temperature of the block before coming in contact with the film. In a simpler head design, the chamber containing the wick is eliminated and

\*Phot. Sci. & Eng. 5: 79/86 (1961).

the porous plate accomplishes the dispersion of the solution flow.

An applicator relying on a meniscus of solution formed between a porous roller and the film emulsion was described by E. D. Seymour.\* The applicator roller is a hollow stainless steel tube plugged at both ends with small holes drilled radially through the roll and with die-cut Dacron felt washers slipped on the tube and retained by axial pressure of a collar. The processing solution, preferably a monobath, is brought first to the required temperature and then forced under pressure into the applicator tube through small holes in the bearings that coincide with similar holes in the applicator tube. From there it flows out through the Dacron felt washers to contact the emulsion.

#### JET SPRAY AND SLIT PROCESSORS

For the Kelvin Hughes system of rapid processing the Venturi-type jet spray system was adopted. This is operated by compressed air.† Atomised droplets of the various solutions are sprayed onto the emulsion at high velocity and at an economical rate. As this is a "total loss system", results are constant and no replenisher system is required. For reasons of economy the jet profile is elliptical instead of round and this has been achieved by the use of twin air jets.

Jet spray techniques were considered unsuitable for the airborne processor because of the problems associated with condensation of spray mist and the question of successfully sealing a continuously moving film. Thus a processing "slot" was devised‡ and this is a unit made in Inconel or Hastelloy "C", consisting of a bar of material with three slots accurately machined therein. Two of these slots carry the processing fluids and, thus, have an inlet and outlet feed and return, but the centre slot is not so provided since its function is to separate the developing slot from the fixing slot by ensuring an area of ambient pressure between these. Each slot may be regarded in itself as an open weir, which, when placed close to the emulsion surface of the film, forms a closed channel through which the processing fluid is drawn in contact with

\*Edgar D. Seymour, *Phot. Sci. & Eng.* 2: 91 (1958).

†R. C. M. Smith and E. R. Townley, *J. Phot. Sci.*, 7, 55 (1959).

‡E. R. Townley, *Phot. Sci. & Eng.*, 6: 26 (1962).



the emulsion surface. Since this fluid is drawn through the channel by negative pressure, it becomes a leak-proof system, which is consistent with airborne requirements of altitude and attitude.

The film is transported past the slot where it is fully developed at a temperature of 40°C. in a time of 2 seconds; it then passes a narrow ambient air channel after which it is fixed via a slot similar to the developer channel in a similar time. Thus, the record is available with an access time of only 5 seconds. It should be appreciated that this applicator is arranged transversely to the film motion and is so aligned that there is a small air cushion between the emulsion and slot surfaces, ensuring turbulent liquid flow in the slot channel and at the same time preventing damage to the emulsion surface. Further, the emulsion is effectively squeezed as it leaves the slot glands.

#### ROLLER APPLICATORS

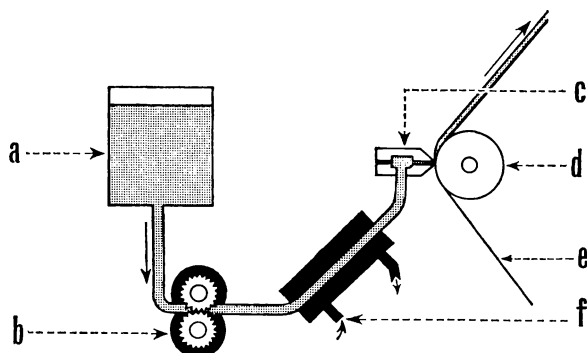
Processing solutions can also be applied to the emulsion surface by non-porous rollers or wheels. Such a processor is the U.S. Signal Corps wheel processor which has three roller applicators for continuous rapid processing at an approximate rate of 100 ft. per minute.\* Normally this machine works with three tanks, but its principle is adaptable to various processing techniques. It is claimed that this processing technique can halve the processing time in comparison with immersion processing under the same temperature and bath conditions. The three applicator wheels are so arranged that they are sequentially contacted along a portion of their periphery by the emulsion side of the film. The rollers are driven in a contrary direction to the motion of the film.

A similar device was constructed by J. C. Barnes and L. J. Fortmiller.† The lower portion of the rotating drum is suspended in the solution and the drum rotates at the rate of 300 r.p.m., in this case, however, in the direction of film travel. A comparatively thick layer of solution is carried round the upper circumference of the drum over which the film is positioned by two small guide rollers. Normally two drums are used. The first drum applies the developer, the

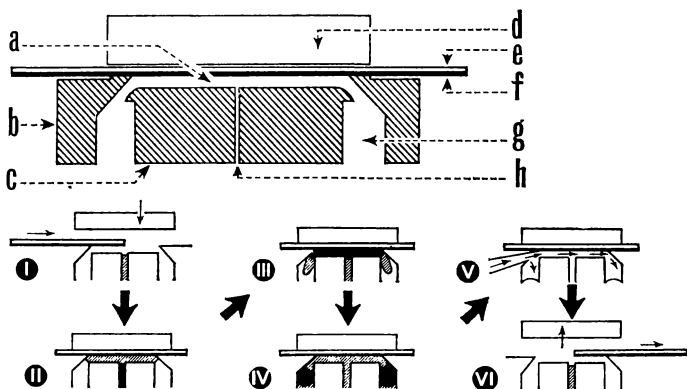
\*S. L. Hersh and F. Smith, *Phot. Sci. & Eng.* 5: 52 (1961).

†*Phot. Sci. & Eng.* 7: 269 (1963).

## RAPID ACCESS PROCESSING



The elements of the viscous solution applicator (above) are:  
 a. Solution reservoir. b. Gear pumps. c. Coating hopper. d. Back-up roller. e. Film. f. Temperature control jacket.

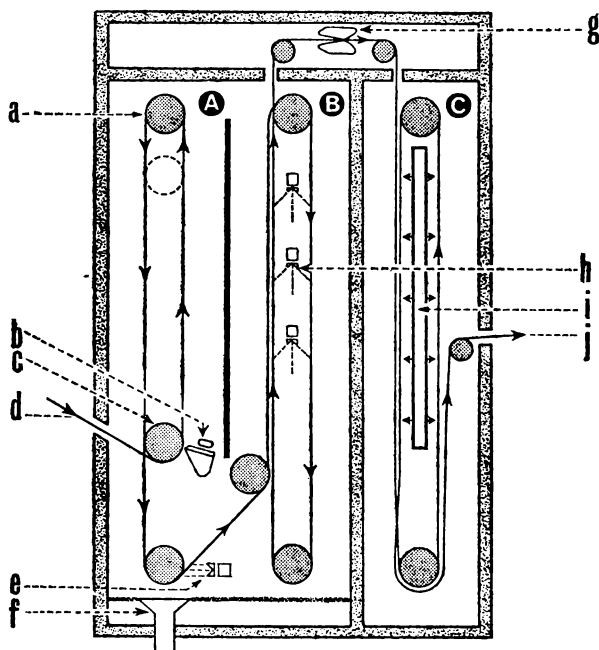


In the capillary chamber processor the film is pressed against an opening of a narrow chamber into which the processing solutions are introduced in sequence.

a. Capillary chamber. b. Sealing frame. c. Heater block. d. Pressure plate. e. Film. f. Film emulsion. g. Overflow well. h. Opening through which solutions are introduced.

At the start of the processing cycle the film moves into position I and is pressed against the sealing frame. Then follows II, development; III, fixing; IV, washing; V, drying by air blown into the chamber; VI, removal or advancement of the film for the next cycle.

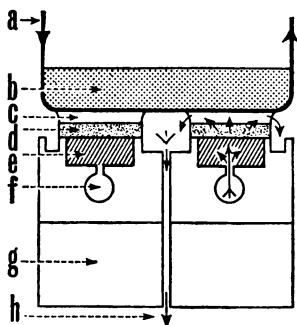
## RAPID ACCESS PROCESSING



In viscous processing, the film passes through a processing chamber 'A' where the viscous solution is applied to the film surface by a coating hopper and from there into the wash compartment 'B' and the drying chamber 'C'. This scheme applies to a monobath solution; with two-bath (development and fixation) processing the wash chamber is followed by a second processing chamber for the fixer and another wash chamber.

- a. Adjustable roller to lengthen or shorten the film path (for longer or shorter development) after the developer is applied.
- b. Coating hopper.
- c. Coating roller.
- d. Entry of film from camera spool.
- e. Cut-off spray to stop development.
- f. Drain.
- g. Air squeegee.
- h. Spray washing nozzles.
- i. Warm air stream.
- j. Exit of film to spooling.

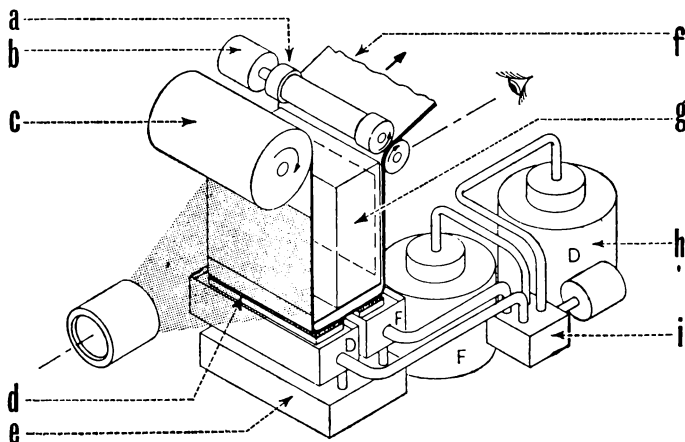
## RAPID ACCESS PROCESSING



In the porous plate applicator the solutions are applied through porous plates in contact with the film surface which moves past the plates.

a. Film. b. Back-up plate. c. Solution meniscus. d. Porous plate. e. Wick. f. Solution. g. Thermostatic heater block. h. Drain.

The unit shown has two applicators for development and fixing respectively.

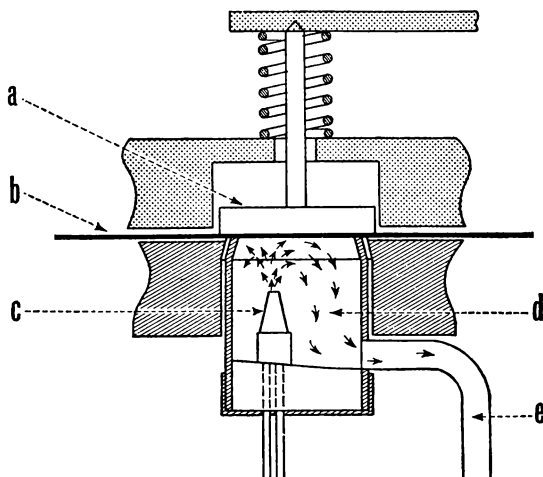


The porous plate applicator is here part of a complete camera and viewing system. The film from the supply roll c travels past the lens which projects the image on it and past the porous plates, running in front of a lamphouse where it can be observed immediately.

a. Film drive. b. Drive motor. c. Film supply. d. Solution meniscus. e. Waste tank. f. Processed film. g. Lamphouse. h. Solution supply tank. i. Pump.

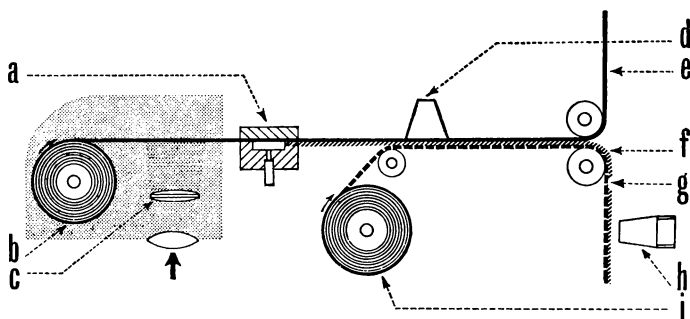
'D' is the developer tank and stage, 'F' the fixing tank and applicator.

## RAPID ACCESS PROCESSING



The jet spray processor is again a chamber system where the chemicals are sprayed on to the film surface held against a spray chamber.

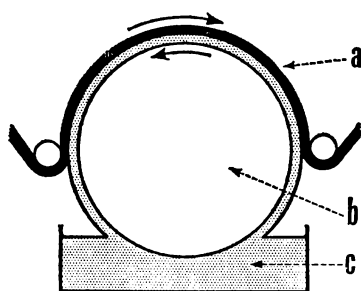
a. Pressure plate. b. Film. c. Jet. d. Jet chamber. e. Waste outlet.



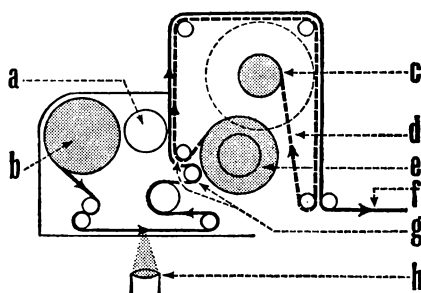
In the negative-positive rapid access system, the film, after exposure in the camera unit (shown shaded), passes a viscous solution applicator. A positive film is then pressed into contact, emulsion to emulsion with the negative, and this sandwich runs in front of a printing light which prints the negative on to the positive where it is immediately developed.

a. Solution applicator. b. Negative supply in camera. c. Camera lens in exposure station. d. Printing light. e. Negative after separation of sandwich. f. Processing solution layer. g. Positive film. h. Viewer. i. Positive film supply.

## RAPID ACCESS PROCESSING



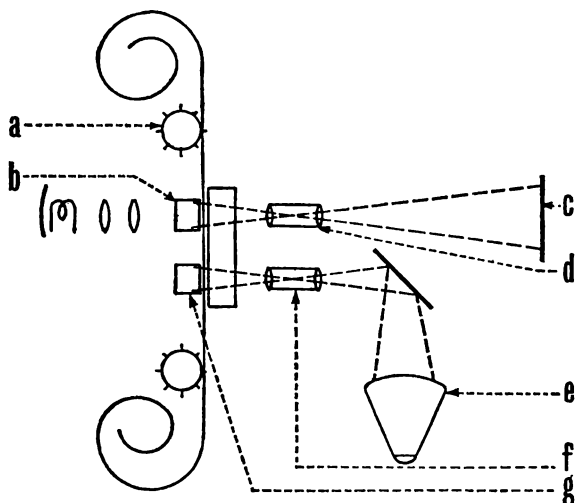
With non-porous roller applicators the film 'a' is stretched over the top of a fast-rotating drum 'b' which dips into a solution tray 'c' to carry the solutions to the film surface. Each processing station has a similar applicator. The film travels at ten feet per minute.



Saturated web processing involves the use of a suitable absorbent material acting as the intermediate carrier for the processing solution. Equipment utilising the saturated web is leakproof, requires no pumps, valves, metering devices or complex machinery. In operation, the web is pre-saturated with aqueous processing solution such as a monobath and then brought into intimate contact with the emulsion surface of the film.

a. Motor. b. Film in camera. c. Take-up spool for web. d. Web. e. Supply of saturated web. f. Processed film. g. Sandwiching rollers. h. Camera lens recording image.

## RAPID ACCESS PROCESSING



This apparatus takes a photograph from a cathode ray presentation, processes it automatically and then projects it immediately. The machine is designed for two solution processing and the drawing shows the relative position of the developing chamber and the transparent fixing chamber.

a. Transport sprockets. b. Transparent fixing chamber. c. Screen. d. Projection lens. e. Cathode ray tube. f. Camera lens. g. Developing chamber.

second one the fixer. The film then passes over a spacer roller into a washing tank and finally past a squeegee into a simple drier. The speed of the operation is variable so that various times of treatment from 1-10 seconds can be produced.

#### SATURATED WEB APPLICATORS

Saturated web processing involves the use of a suitable absorbent material acting as the intermediate carrier for the processing solution. For this system, a number of advantages are claimed.\* The volume of solution used is very small, approximately equal to the volume of the material to be processed. Each area of emulsion is processed with fresh solution. Undesirable by-products of the reaction are removed with the web upon its separation from the processed film. The web is adaptable to various processing formulations, i.e. monobath as well as standard 2 stage processing. Equipment utilising the saturated web is leakproof, requires no pumps, valves, metering devices or complex machinery. However, the selection of a suitable web material offers a number of problems. If paper is used, fibre markings appear in the negative. For the Raproroll system a special paper is used made of fine fibres in a sheet of high porosity permitting uniform compression. Paper alone has insufficient web strength and it is therefore used bonded to a non-porous plastic film. This laminated backing gives it not only high tensile strength, but decreases also the chance of entrapping air and makes the processing solution available from one side only. It also serves as an evaporation and oxidation barrier.

In operation the web, pre-saturated with an aqueous processing solution such as a monobath, is brought into intimate contact with the emulsion surface of the film. Contact between the web and the emulsion is accomplished by winding the surfaces together under tension around a portion of the periphery of a drum. After processing is complete, the web is stripped away from the developed film.

#### “DRY” DEVELOPMENT

Rapid dry development of oscillograph traces in a silver-sensitised recording paper has been achieved by P. H.

\*Seymour Schreck, *Phot. Sci. & Eng.* 4: 298 (1960).



Stewart, W. Bornemann and W. B. Kendall\* using a processor of simple design. The paper contains all the necessary developer chemicals incorporated in the emulsion. The processor is a heating chamber entirely enclosed, except for slits at the front and back for exposed material to enter and leave. Processing is initiated by moisture driven from the emulsion and base which condenses on the cool surface of the entering emulsion. The combination of increased moisture and rapid application of heat causes development to occur within a few seconds.

The machine is built to develop 12 in. wide rolls of paper and consists essentially, of a chamber completely enclosed, except for provision for the paper to enter and leave. The curved bottom plate is of smooth metal and is equipped with four 350-w. heaters along its 21 in. length. The roof is another metal sheet, spaced just 0.5 in. above the bottom plate, and is equipped with four 160-w. heaters. A pair of drive rolls is located just below the exit to pull the paper through the processor. When the machine is operating at the rate of 25 ft./min. or less, the temperature of the bottom plate is usually adjusted to about 240°F. At higher speeds, however, bottom plate temperatures as high as 300°F. may be required to ensure sufficiently rapid transfer of heat from the plate to the emulsion layer through the paper base.

Prints prepared according to the methods outlined are, of course, unfixed. Furthermore, the developer remaining in the background areas is still essentially as active as it was before the paper was processed. Consequently, if the prints are fogged by exposure to ambient light, the background tends to darken because of developing and printing out. Nevertheless, these unfixed prints may have considerable utility, for instance for recording oscillographic traces.

A processing technique similar to the above is flash processing, described by J. H. Jacobs.† The developer is applied in a very thin layer to the emulsion side only of the recording medium which is then run over a hot surface. The heat applied through the back causes rapid development and drying. The record can then be viewed in daylight or subsequently be stabilised or fixed if required.

\*Phot. Sci. & Eng. 5: 113/114 (1961).

†Phot. Sci. & Eng. 1: 156 (1958).

## “PHOTO” DEVELOPMENT

The need in modern engineering developments for materials to record data at very high speeds and the need to obtain access to such data in a minimum of time and with a minimum of chemical processing has led to the development of a new class of direct-writing recording materials. H. D. Hunt\* reported on these new products which have the unique ability of being processed entirely by radiant energy with no liquid or chemical steps. The developed image can be viewed within 1 second of recording when the proper energy sequence is followed.

The rapid writing speed of these new materials is obtained by enhancing the ability of the silver halide crystals to form internal latent images at high intensity in extremely short exposure times, for it is the internal latent image, rather than the surface latent image, that is intensified subsequently by absorbed radiant energy.

In the amplification or development of the latent image to a visible form, also called “post-exposure intensification” or “photo” development, the energy used is the light absorbed by the silver halide in a second exposure rather than energy released by the reducing agents in normal chemical development. This light is ultraviolet and blue light, but must be of lower intensity than the exposing light. However, the energy absorbed—that is the intensity multiplied by the time—in this step is much greater than that used in forming the latent image. The intensity and time of exposure are in the region where little or no new internal latent image will be formed. This low-intensity amplification exposure, in addition, forms surface latent images on the non-image grains, i.e. on those which did not receive the high-intensity initial exposure. These surface latent images apparently inhibit or prevent the formation of internal latent images. As a result the background is desensitised and is not easily darkened by further exposure to either high- or low- intensity radiation.

To review the sequence of events that occur when this emulsion is used: first, the initial exposure is made with a high-intensity (usually UV) light source to form an internal latent image. Following this the paper is given an exposure to light at a lower intensity for a longer period such as

\*Phot. Sci. & Eng. 5: 104/8 (1961).

normal room light. During this second step, only the grains which were originally exposed become blackened while the remaining grains are desensitised by the low-intensity exposure.

#### DRY SILVER PROCESS

Another process that leads to the formation of an image without any wet chemical processing stages is the 3M Dry Silver Process described by B. R. Harriman.\* This process uses a heat development stage for forming the visible image in a specially designed light sensitive material. The material consists of a silver halide as the light sensitive element, a source of silver in the form of a silver soap or behenate, a developer or reducing agent all contained in a film-forming binder and coated on an inert support. It can be seen that this process is similar in principle to conventional photographic materials except that all the chemicals required for image formation are contained in the material itself and after exposure, development or amplification of the latent image is brought about by heat and no fixing stage is required.

The thermal development of this dry silver material generally is carried out at relatively high temperatures (80-120°C. for 5-20 seconds) and so yields an image within a very short period of time. A further fixing stage is not required because development is unlikely to continue at normal temperatures although there may be some additional latent image formed. At the present time the fastest dry silver material commercially available is a green sensitive material with an ASA speed of 0.1 coated on a paper base which is used for recording cathode ray tube images.

The heat development of coatings of a silver soap forms the basis of the 3M Dry Copiers. A separate foil containing the reducing agent is used for the exposing step in contact with the original in which the reducing agent is destroyed by the action of light in areas where there is no image. Heating this foil in contact with a paper coated with the silver soap causes reduction of the silver soap to silver to form a positive copy of the original.

\*Unconventional Photographic Systems, S.P.S.E. Symposium (1967).

## CHEMICAL TRANSFER PROCESSING

The chemical transfer process makes it possible to produce negatives and prints in a matter of seconds either direct in the camera or in special machines for document reproduction.

The emulsion layer of the material used for this process is similar to that of a normal photographic emulsion. The positive paper has a gelatine layer, but instead of the silver halides it contains so-called "nucleating" agents which are capable of accelerating the conversion of dissolved silver halide into metallic silver. The process depends therefore on the presence of sodium thiosulphate as a silver halide solvent. When the developed negative is squeegeed into contact with this positive paper, the hypo dissolves the unchanged silver halide in the un-exposed image areas, but no such action takes place in areas where the silver halides have been developed to silver. When the developer-hypo solution diffuses from the negative emulsion layer into the gelatine layer of the positive paper, it encounters the nucleating agents which may consist of colloidal silver. The dissolved silver halides are precipitated in the form of black metallic silver thus forming a black positive image on the positive paper. The gelatine layers of the negative and positive materials are so thin and the distances travelled by the solution so small that no significant sideways diffusion takes place. A sharp well-defined reproduction is obtained when the sheets are stripped apart.

This principle has been developed by E. H. Land for the one-minute Polaroid camera and by Rott and Weyde for document reproduction. In the Polaroid camera a finished positive print is directly produced in the camera itself immediately after exposure. The roll film consists of two paper strips, one coated with a light sensitive negative type emulsion, the other with a layer containing nuclei for precipitating silver during simultaneous development of the negative and positive images. The two paper strips travel through the camera independently at first but are brought in contact after exposure of the negative layer. Pods of developing agent attached at appropriate intervals along the positive paper strip are ruptured when the two strips are pressed into contact between metal rollers and form a very thin layer of developer between the two strips. After a processing period

of 10 seconds, a door is opened at the back of the camera and the positive print, and in some of the systems also the negative, can be pulled out.

For document reproduction the material is used in the form of sheets and the negative material and positive material is handled separately. The negative paper is first exposed and then inserted together with the positive paper into two closely spaced slots of the developing machine. The two sheets of paper pass through a container of developer solution being held apart by a series of guides or channels. On emerging from the developer, the sheets pass between a pair of revolving rollers which complete the transport of the paper through the developer, squeegee the sheets into contact with one another and eject them from a single exit slot. The sheets are then stripped apart by hand to separate the copy from the negative paper.

The principle is also used in the Kodak Bimat\* system which employs a transfer film pre-soaked by the manufacturer or bought dry and soaked by the user in the solution provided. Fairly simple apparatus yields both a negative and a positive by the mechanism described previously.

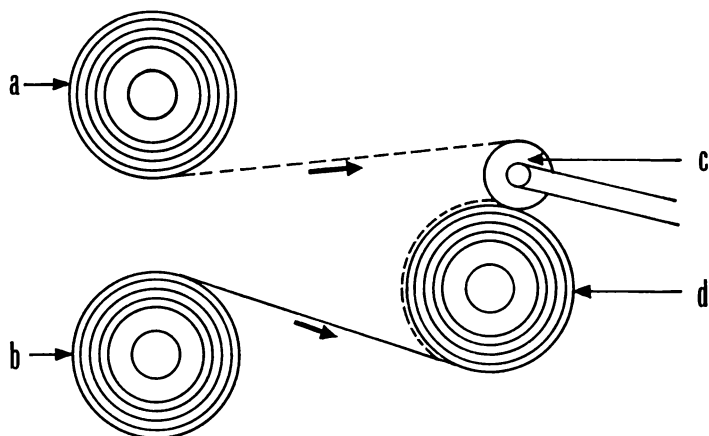
It is a semi-wet process and no additional solutions are required by the user unless stable images are required, in which case the films should be washed and dried in the normal manner. Even without washing it is claimed that these films are stable for several months if stored dry.

The pre-soaked transfer film and the exposed negative may be wound on to a roller where the transfer and development takes place as shown in the diagram on page 320. After the recommended time (90 seconds to 20 minutes at 60°-100°F.) the tacky films are unwound, stripped apart and dried. The process is self-limiting so that these times represent minimum times but the exposed and transfer films must not be allowed to dry in contact with each other or stripping apart becomes impossible.

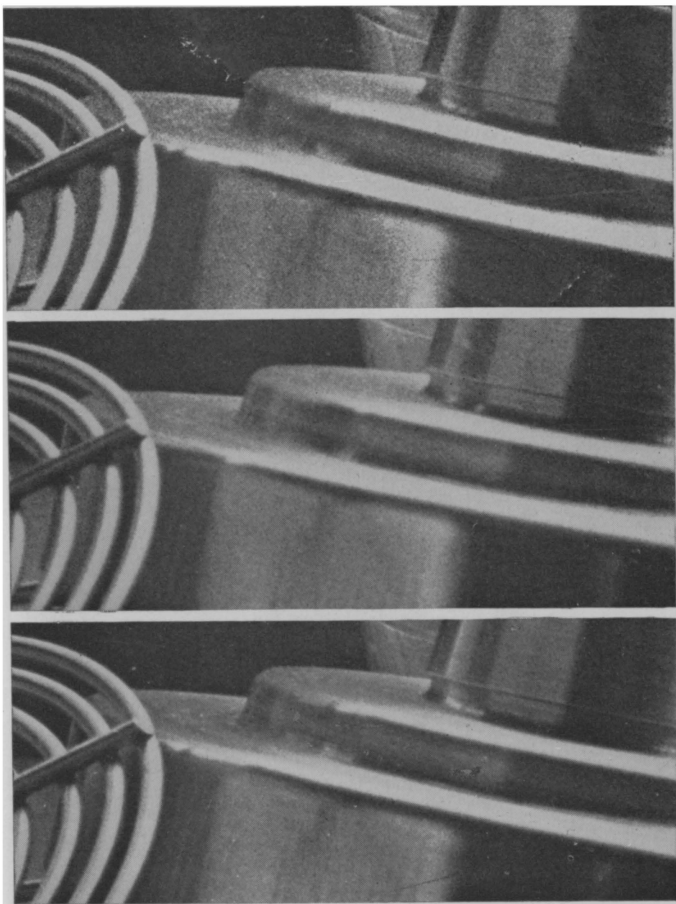
Access times as low as ten seconds are claimed for cathode ray recording film using a continuous process but the negative is normally discarded. This system has obvious advantages for aerial reconnaissance work where solutions would be impossible to use or in places where water is unavailable.

*\*An Introduction to Kodak Bimat Transfer Processing System, Kodak Pamphlet No. P-65, R. P. Mason, S.P.S.E. News, 9 (2) 8, (1966).*

## KODAK BIMAT SYSTEM



The elements of the Bimat system are: a. Reel of Bimat film. b. Reel of negative film. c. Pressure roller. d. Wind-up spindle.



**FINE-GRAIN DEVELOPMENT.** The developer has a very important influence on the grain of the negative. The naked eye may fail to detect grain or graininess, but enlarging will reveal it. A section of a negative was here developed 1. (*top*) in ordinary developer (p. 174), 2. (*centre*) normal fine-grain developer (p. 206), and 3. (*bottom*) a super-fine grain developer (p. 210).



INTENSIFICATION. The negative was badly underdeveloped but still showed all the essential detail; the density was, however, so low that even an extra-hard paper failed to produce a satisfactory print (*top*). By intensification (see page 347), however, a reasonably normal result (*bottom*) was obtained.—*H. Gorny.*

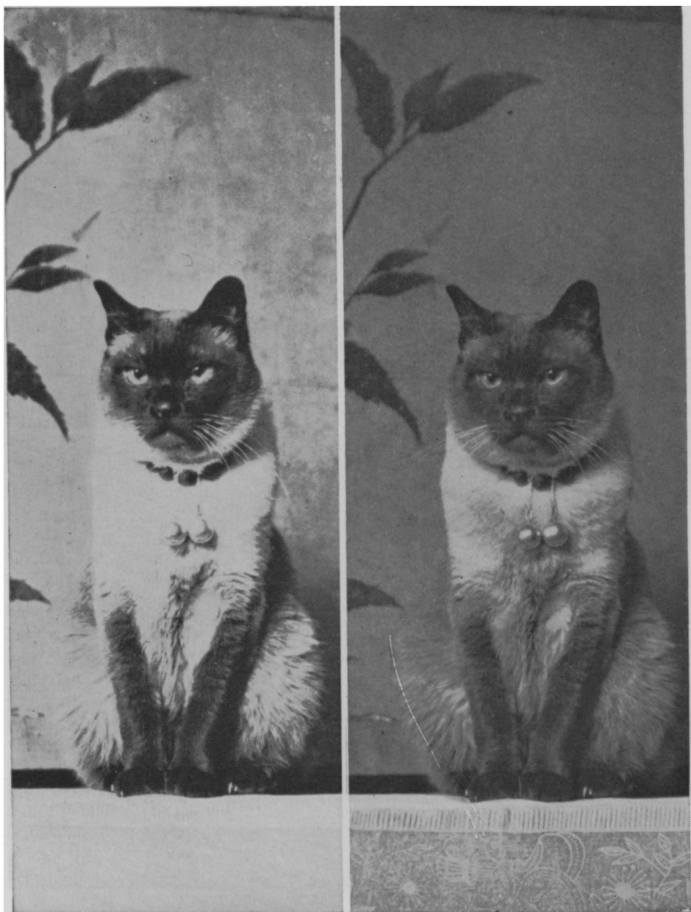




PROPORTIONAL REDUCTION. The negative was dense and contrasty, so that even when a soft paper was used the result was too hard (*left*). By the use of proportional reduction (see page 343) the negative was notably improved and (*right*) a good print obtained on a soft paper.—*H. Gorny.*



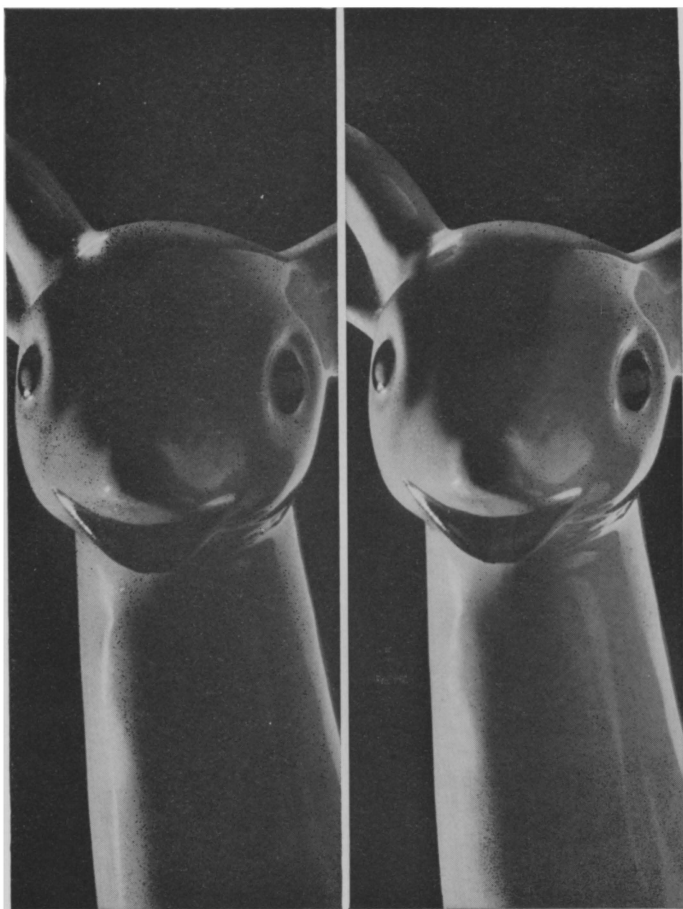
**SUBTRACTIVE REDUCTION.** The negative as a whole was somewhat too dense and was rather strongly fogged in the shadows (*left*). By the use of Farmer's reducer (see page 342) the fog was removed and the whole negative brightened up (*right*).—*H. Gorny.*



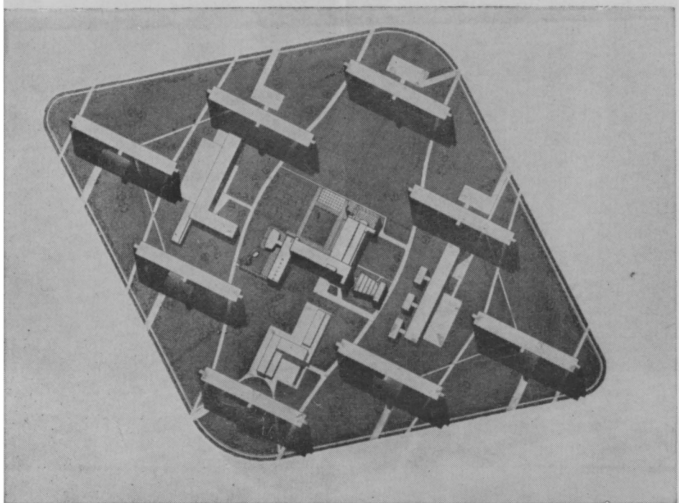
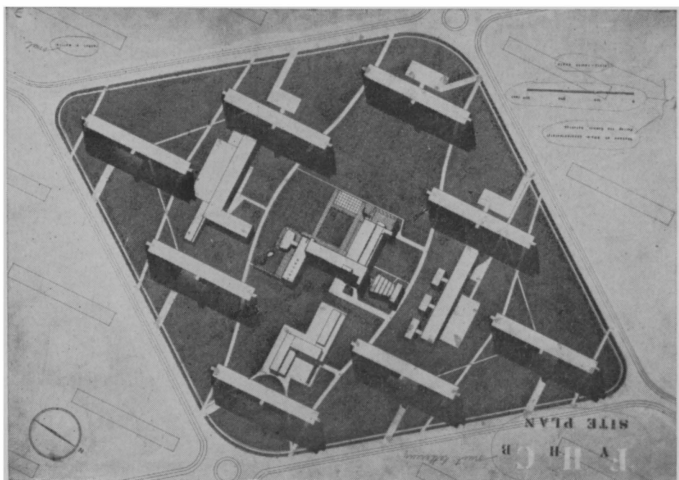
**SUPER-PROPORTIONAL REDUCTION.** The fault in the negative was mainly too dense highlights, whereas the rendering of the shadows was approximately correct (*left*). The treatment called for was the reduction of the highlights and so a super-proportional reducer, ammonium persulphate (see page 344), was chosen.—*H. Gorny.*



**PARTIAL REDUCTION.** The sky in the negative appeared almost opaque and would therefore print as a white expanse. As the negative was not suitable for treatment with the ammonium persulphate reducer, the process of partial reduction described on page 355 was used because in this case one had a single well-defined area which was comparatively simple to operate upon.—*Alexander.*



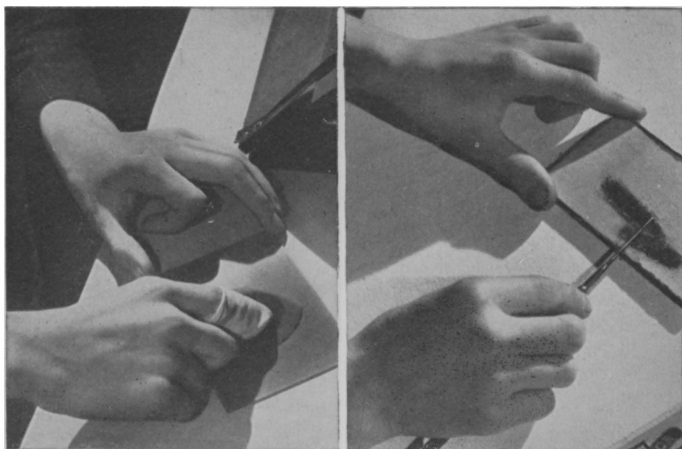
**PARTIAL INTENSIFICATION.** The highlights of the negative were well defined and the shadows had detail, but insufficient to provide a really good print or enlargement. An all-over intensification of the negative would have emphasised the highlights too much, so a partial intensification (see page 355) of the shadow areas was carried out.—*Alexander.*



**BLOCKING OUT.** This process, which is described on page 356, can be used particularly for emphasising the more important parts of a subject. It may be employed to hold back or to suppress entirely some unwanted portion of the background by blacking it out as seen in the *lower picture*.—*Polytechnic of Central London.*



**RIGHT AND WRONG METHODS IN RETOUCHING.**  
*Left top.* The right attitude and arrangement when retouching. The retouching desk is so arranged that it is evenly illuminated by light reflected from the mirror behind it, while the eyes of the operator are protected by the shade projecting from the frame of the desk.



## TWO IMPORTANT OPERATIONS IN RETOUCHING.

*Left.* Applying the varnish (see page 361) with the aid of a linen swab before proceeding to retouch with a pencil. The varnish is essential if the pencil is to take on the negative surface.

*Right:* Rubbing down the graphite powder which is to be used in local intensification or retouching. The negative must be treated with a matt varnish before the graphite is applied.—*W. Nurnberg.*

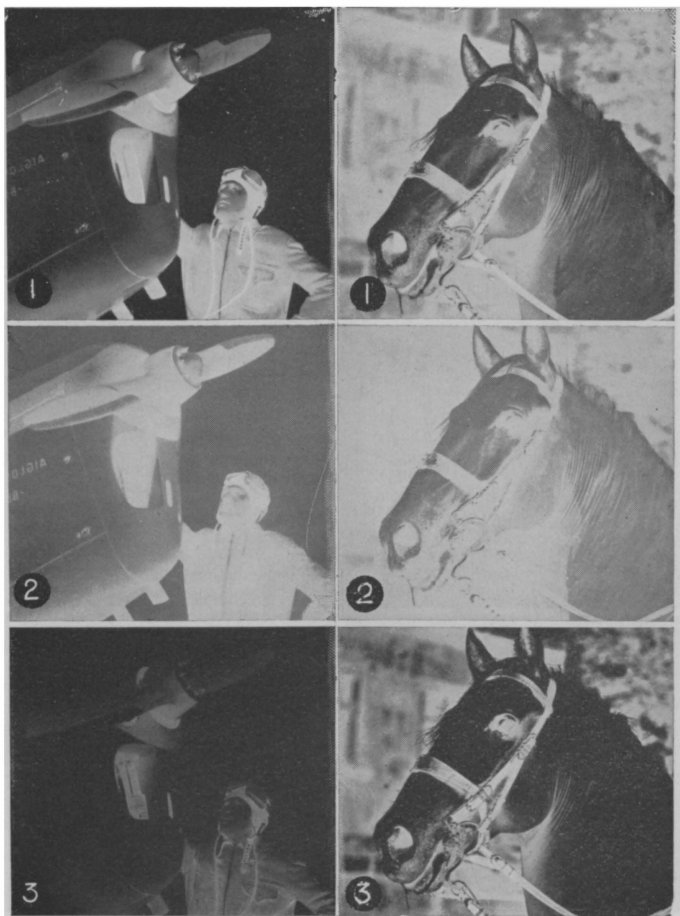
Continued from page 329.

The illustration *top right* shows none of these conditions fulfilled; the angle of the desk is wrong, the position cramped and the eyes subjected to a glaring light.

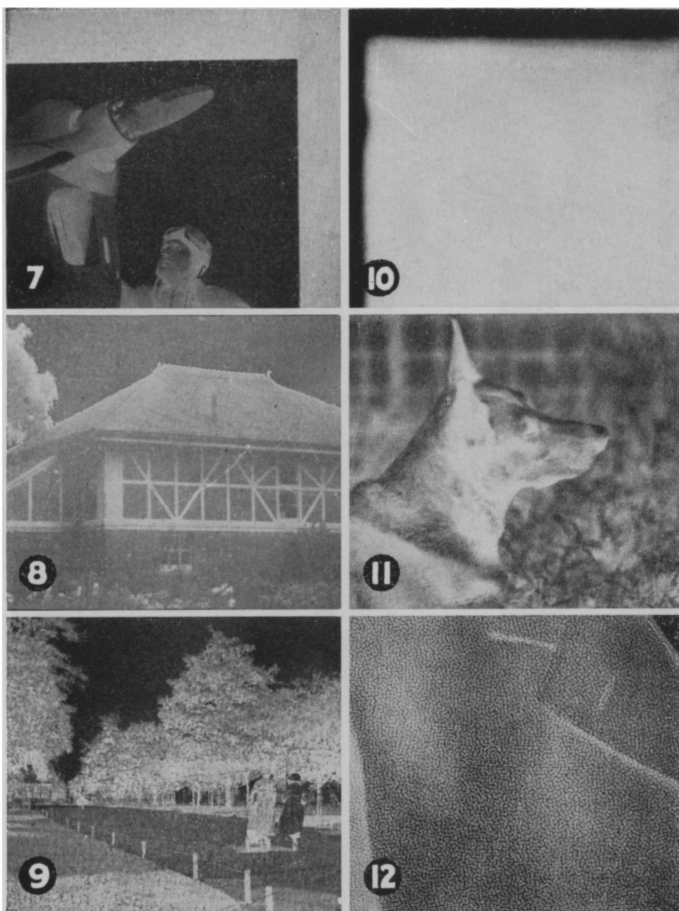
*Left bottom.* The correct method of holding the retouching pencil. It is held lightly and not too near the point; hence the danger of too heavy a stroke is obviated.

*Right bottom.* The wrong way to hold the pencil; it is held too tightly and too near the point. Control is difficult and the strokes will be too heavy.—*W. Nurnberg.*

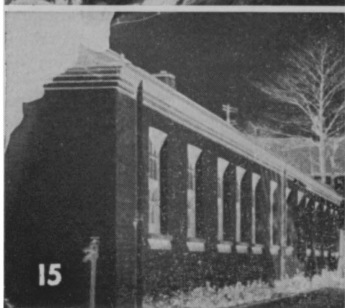




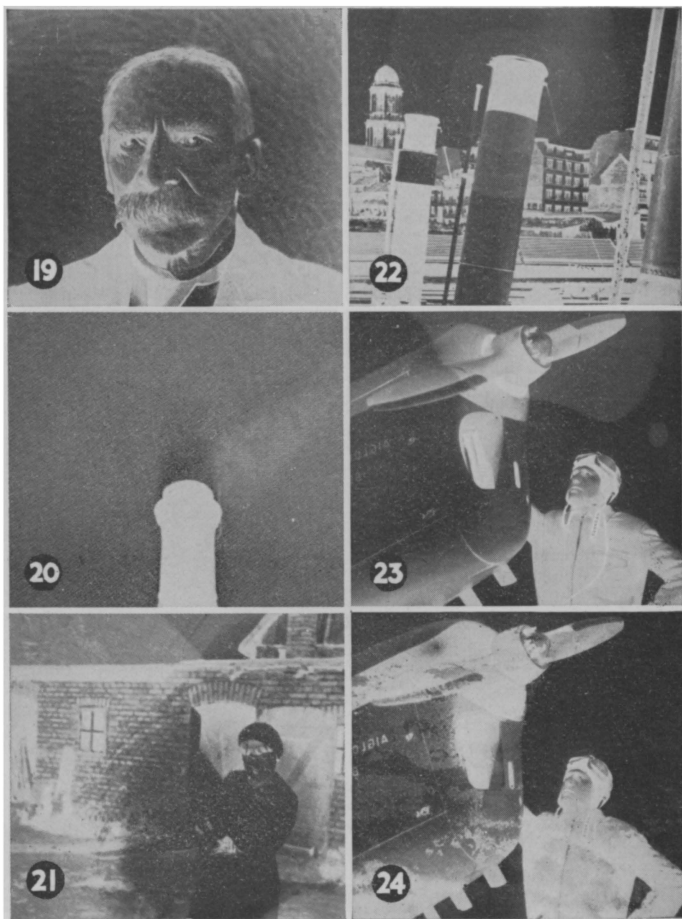
DEFECTS IN NEGATIVES. *Left.* 1. Correct exposure. 2. Under-exposure (p. 404—1). 3. Over-exposure (p. 405—5). *Right.* 1. Correct development. 2. Under-development (p. 404—2). 3. Over-development (p. 404—4).



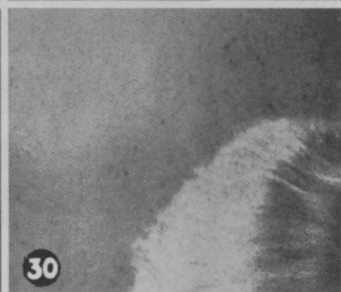
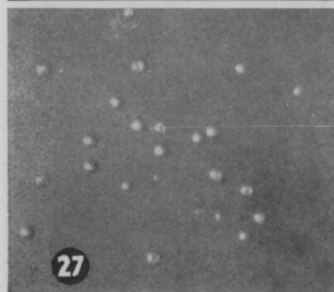
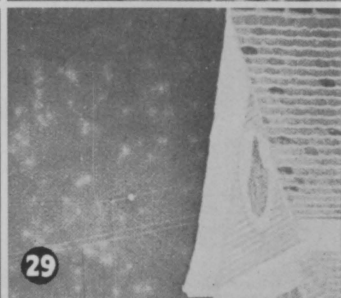
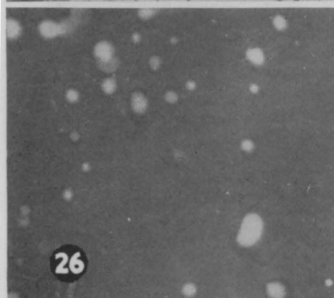
7. Grey fog all over (p. 405—6). 8. Reversal of the negative (p. 410—38). 9. Fogging through backing (p. 405—6b). 10. Black fog on edge of plate (p. 405—7). 11. Reticulation (p. 409—30). 12. Reticulation magnified.



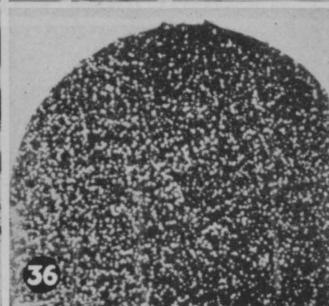
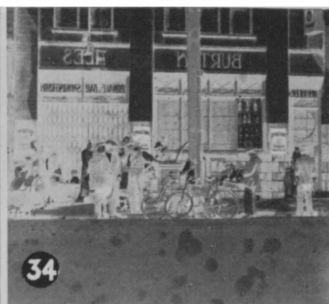
13. Melting due to hot water. 14. Melting (p. 410—39).  
15. Frilling (p. 410—36). 16. Finger marking (p. 410). 17. Marks  
caused by dust brush. 18. Contact during development (p. 410).



19. Irregular density (p. 409—27). 20. Streaks on the negative (p. 408—15). 21. Area of higher density (p. 408—21). 22. Areas of lower density due to adding potassium bromide (p. 408—21). 23. Irregular development (p. 408—18). 24. Stop bath too strong.



25. Air bell marks (p. 409—28). 26. Air bells magnified. 27. Small blisters (p. 410—35). 28. Streaks (p. 408—15). 29. Small flecks (p. 409—26). 30. Dark flecks (p. 410—32).



31. Dust (p. 410—31). 32. Chemical dust (p. 410—31). 33. Drying marks (p. 410—34). 34. Water splashes (p. 410—34). 35. Water splashes (p. 410—34). 36. Holes in the film (p. 410—33).

## COMBINED CAMERA-PROCESSORS-VIEWERS

In many cases it is important to shorten the time between photographic recording of information and its presentation for visual inspection either in a permanent or temporary form. This can be achieved with combined camera-processors-viewers or -projectors.

A system for projection of the photographic data recording within a fraction of a second after exposure has been developed by C. Orlando.\* The equipment (page 313) takes a photograph from a cathode-ray presentation, processes it automatically and then projects it immediately. The machine is designed to use two solution processing which in this case gives results superior to those obtainable with monobath processing. It is possible to process a film within 0.2 seconds at 185°F. and to fix it in approximately 0.2 to 0.3 seconds at 205°F. The schematic drawing on page 313 shows the relative position of the developing chamber and the transparent fixing chamber. A similar device was described by R. P. Mason.† His radar recording equipment employs a porous applicator which is inserted in a narrow space between a camera portion and the viewing station (page 310) using a U-shaped film path in a relatively small piece of equipment. A machine has also been designed which provides both negative and positive in a rapid processing operation. A sandwich is formed between the exposed negative and a positive film with a processing solution in between. The processing solution is a monobath. It develops the negative which is immediately printed on the positive material and thus developed by the same monobath. The processing solution develops and fixes the positive image almost immediately. The positive and negative films are then separated and either of them can be used in the usual way.‡

## FORMULAE FOR RAPID PROCESSING

Rapid access processing requires highly active developers which make full use of all means to accelerate the developing process, such as high general concentration, pH and temperature. In cases where temperatures considerably exceeding

\*Phot. Sci. and Eng, 2: 142 (1958). U.S. Patent 2856829.

†Phot. Sci. and Eng. 5: 79 (1961).

‡Fairchild Camera & Instrument Corp., Brit. Pat. No. 884,391 (1961).

normal working temperatures are employed, special "quick-finish" (rapid access) films have to be used which stand temperatures up to say approximately 200°F. (93°C.).

Some of the machines described in the foregoing use "monobaths", i.e. Table LVIII.

In cases where the two solution technique is used, a fixing formula based on ammonium thiosulphate should be chosen. For certain specific uses, however, where permanence of the photographic record is of less importance and where it is desirable to produce it in the least possible time, the so-called "stabilisation technique" is applied. This is based on the use of a stabiliser which renders the undeveloped silver halide relatively inert to the effects of heat, light and moisture. The main stabilising agents used for this purpose are: Ammonium thiocyanate and thiourea ammonium thiocyanate approximately 20% solution, thiourea in about 3% solution. Prints stabilised in this way are not to be washed (see page 296).



## *After Treatment of the Negative*

The correcting of negatives by after treatment, in particular by reducing or by intensification, has lost much of its former importance. This is mainly because a satisfactory print can be made from almost any negative on one or other of the many grades of paper now available. Moreover, the very notable latitude in exposure and in manipulation of modern negative material makes the really poor negative a comparative rarity.

Hence the correction of a negative by chemical treatment is called for only in exceptional cases, or when the negative has to be suited to some special positive material which is only available in a restricted range of contrasts. A particular case which may arise is the preparation of lantern slides or diapositives, for here the material available does not appear in a wide range of contrasts.

### REDUCTION

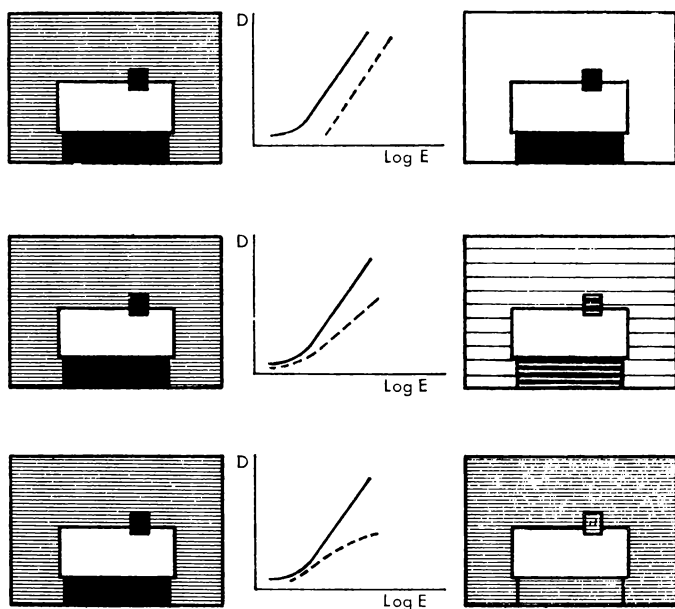
All reducers are oxidising solutions, they either oxidise the silver to a soluble salt or contain a solvent for the silver salts if these are insoluble in water. The permanganate, dichromate, ferric ammonium sulphate, ceric and persulphate reducers are used in the presence of sulphuric acid, forming silver sulphate which is soluble in water. Ferricyanide is used with hypo or thiocyanate to dissolve the silver ferrocyanide which is formed but not soluble in water.

The object of reduction is, as its name implies, the reducing of the density of a negative; it may be the correcting of over-exposure or over-development. Errors in exposure or development may display themselves in various ways in the negative and variously affect its character. The choice of the right reducing agent to use in any particular case will go

far to bring about the necessary correction. The way in which various reducers act is shown on page 341, where the gradation of various negatives is shown diagrammatically in the form of a stairway of densities. They give a section through the film of the negative showing the three steps of varying heights representing shadows, middle tones and highlights. The various reducers can act in three different ways which we will now describe.

- (1) The reducer removes the same quantity of deposit from shadows, middle tones and highlights. It planes down the surface of the negative deposit evenly (page 341), and to this type of reducer we give the name subtractive. As the diagram shows the greatest effect is in the shadows, less in the middle tones and least of all in the highlights. Hence the general effect is to increase the general contrast of the negative. Reducers of this type are Farmer's (see page 342) and Belitzki's (see page 343). They are particularly adapted for reducing negatives where the shadows want clearing and where a general increase in contrast is desirable, as is particularly the case with over-exposed negatives.
- (2) The reducer acts proportionally to the amount of silver present, that is it removes but little from the thin parts, more from the middle tones and most in the heavy densities (see page 341). From the diagram it will be seen that the action results in a notable reduction in the density of the whole negative, the total density of which may be reduced to about one half. It might be said to represent the opposite of over-exposure where, as we have seen (see page 34), increasing length of development gives increased density without notably increasing the contrast of the negative. Reducers of this type are called proportional, and the best known examples are potassium permanganate (see page 343), and mixtures of permanganate and ammonium persulphate (see page 343). These proportional reducers are used to correct over-developed negatives, or all those in which the densities are too heavy.

## REDUCTION



Reduction consists of reducing the density of the negative. Reducers can act in several ways, as the diagram shows. The middle series shows the effect of three types of reducer on the sensitometric curves. The solid lines represent the negative before reduction and the dotted lines represent the negative after reduction. The diagrammatic representation of the house shows the effect of reduction. On the left, the negative before treatment and on the right, after reduction. From top to bottom: First, subtractive reduction. Second, proportional reduction. Third, super-proportional reduction.

- (3) The reducer attacks the heavy parts of the negative more strongly than the middle tones and lighter parts (see page 341). It is called super-proportional for it tends towards a reduction of the general contrast and so is suitable for improving negatives which are too contrasty. That applies particularly to those which have had a short exposure and been over-developed. In such cases it is important that the details in the shadows are not attacked because, by reason of the under-exposure, they are already very thin and weak. Reducers of this type comprise: Ammonium persulphate (see page 344). Benzoquinone (see page 345). Re-development (see page 345). Bleaching processes (see page 346).

#### SUBTRACTIVE REDUCERS

The best known and most widely used subtractive reducer is Farmer's solution. It is almost always kept in the form of two stock solutions.

##### 220.—FARMER'S REDUCER

A. Hypo cryst.	1 ounce	25 grams
Water up to	10 ounces	250 ml.
B. Potassium ferricyanide	$\frac{1}{2}$ ounce	12.5 grams
Water up to	5 ounces	125 ml.

Immediately before use take 4 ounces (100 ml.) water, 4 ounces (100 ml.) of solution A and 2 drams (6 ml.) solution B and mix well. The action of the reducer depends upon the proportion of solution B, the more B is present the more rapid the action, but the strength given above is convenient for good control of the process.

*Caution:* The stock solutions keep indefinitely, the mixed solution has very little keeping power.

The reducing should be watched carefully. It is best to treat the negative for about 20 seconds in the reducer, then rinse well and examine, repeating the operation until the required reduction has been reached. Reduction can be undertaken immediately after the negative has been fixed,

only a short wash being necessary before placing the negative in the reducing bath. When reduction is complete the negative is well washed and dried. Such reduced negatives always show a shiny surface due to the silver having been removed from the outside layer of gelatine.

Belitzki's reducer works in a similar manner to Farmer's.

#### 221.—BELITZKI'S REDUCER

Ferric chloride cryst.	$\frac{1}{4}$ ounce	6.5 grams
Potassium or sodium oxalate	$\frac{1}{2}$ ounce	12.5 grams
Sodium sulphite anhyd.	160 grains	8 grams
Water to make	8 ounces	200 ml.

Before use add 60 grains (3 grams) oxalic acid crystals, shake well until the solution turns green, allow to settle, pour off the supernatant liquor from the crystals and add 2 ounces (50 grams) hypo crystals. For use take one part of this solution and dilute with 11 parts of water.

#### PROPORTIONAL REDUCERS

The following formula is midway in properties between subtractive and a true proportional reducer.

#### 222.—PERMANGANATE REDUCER

A. Potassium permanganate	40 grains	2 grams
Water to make	20 ounces	500 ml.
B. Water	20 ounces	500 ml.
Sulphuric acid conc.	20 minims	1 ml.

Immediately before use take 4 ounces (100 ml.) of water and add 2 drams (7 ml.) each of A and B.

To produce a correctly proportional reducer potassium permanganate is combined with ammonium persulphate as follows:

#### 223.—PERMANGANATE-PERSULPHATE REDUCER

A. Potassium permanganate, 1% solution	$\frac{1}{2}$ ounce	12.5 ml.
Sulphuric acid, 10% solution	$\frac{1}{2}$ ounce	6.5 ml.
Water to make	20 ounces	500 ml.
B. Ammonium persulphate	$\frac{1}{2}$ ounce	12.5 grams
Water to make	20 ounces	500 ml.

For use take 1 part A, 1 part B and 4 parts of water.

If in either of the above cases the negative shows a brown stain after reduction, this can be removed by immersion in the following:

## 224.—STAIN REMOVER

Sodium sulphite anhyd.	6 ounces	150 grams
Oxalic acid	1 ounce	25 grams
Water to make	40 ounces	1000 ml.

## SUPER-PROPORTIONAL REDUCERS

The property of reducing the denser parts of the negative in preference to the middle tones and shadows is possessed in an unusual degree by the ammonium persulphate reducer. Ammonium persulphate is, however, notably subject to deterioration on keeping and is also easily affected by other substances; hence successful control of reduction when using it requires special precautions. The usual solution used consists of:

### 225.—AMMONIUM PERSULPHATE REDUCER

Ammonium persulphate	50 grains	2.5 gram
Sulphuric acid, 10% solution	20 minims	1 ml.
Water	4 ounces	100 ml.

If the tap water contains chloride or lime salts distilled water should be used. Also when fresh the crystals of persulphate crackle as they dissolve; if this does not occur the freshness of the persulphate is suspect and the action of the reducer will be lessened or may be absent.

Some workers prefer as an alternative solution the following:

### 226.—ALTERNATIVE AMMONIUM PERSULPHATE REDUCER

Distilled water	4 ounces	100 ml.
Ammonium persulphate	50 grains	2.5 grams
Ammonia 0.910	40 minims	2 ml.
Hypo	50 grains	2.5 grams

All negatives that are to be reduced with persulphate must be very thoroughly washed. The negative must be carefully watched during the process of reduction, preferably at intervals of not more than 15 seconds. The rate of reduction varies with different materials; with some it is slow, with others very rapid. As soon as the desired degree of reduction is approached the process should be stopped. This can best be done by using a stop-bath consisting of a 12% solution of sodium sulphite.

The negative is given a rinse and placed in this bath for a minute or so and then given a thorough final wash.

Most of the earlier failures with persulphate reducers can be traced to the use of old and partially decomposed, or to impure persulphate. They had the effect, however, of inducing workers to use other methods which were less unreliable. Of these one well used formula is that using benzoquinone.

#### 227.—BENZOQUINONE REDUCER

Water	4 ounces	1000 ml.
Sulphuric acid conc.	60 minims	3 ml.
Benzoquinone	20 grains	1 gram

The well washed negative is treated for 4-5 minutes in this solution.

#### RE-DEVELOPMENT

A useful and controllable method of reducing the contrast of a hard negative is the so-called re-development method in which the negative is just bleached in a suitable bleaching bath and is then re-developed to the desired contrast and density. This is sometimes called harmonising.

What actually happens is that during the so-called bleaching process the developed silver image of the negative is re-converted into chloride or bromide and so can be developed again to the desired gradation and density. For this purpose it is preferable to use a somewhat slow working fine-grain developer; as soon as the required density and gradation are reached the re-developed negative is thoroughly fixed out.

A useful bleaching solution is:

#### 228.—BLEACH BATH FOR RE-DEVELOPMENT

Water	40 ounces	1000 ml.
Copper sulphate	4 ounces	100 grams
Sodium chloride (common salt)	4 ounces	100 grams
Sulphuric acid conc.	1 ounce	25 ml.

Bleaching must be thorough and no trace of the original reduced silver image must remain. When this is accomplished, wash for a few minutes until the image is pure white and re-develop with the following developer.

#### 229.—FINE-GRAIN RE-DEVELOPER

Water	40 ounces	1000 ml.
p-Phenylenediamine	60 grains	3 grams
Sodium sulphite anhyd	1 ounce	25 grams

Development must be carried out until the image is plainly seen through the back of the negative otherwise the gradation will suffer and the negative be too thin. Another developer, somewhat more energetic, which can be used for this purpose is the metol single solution (Nos. 1-3) used well diluted. As a general guide the re-developed negative should appear not very different to the original negative before bleaching. If it is now rinsed and thoroughly fixed it will be found to have distinctly less density and a less steep gradation.

Another interesting method of varying and reducing the contrast makes use of the idea of protecting the silver in the shadows or thin densities of the negative either by depositing there a substance not attacked by the reducer or by converting the silver into a compound which equally is not attacked. To do this the negative is given a superficial bleach in the following bath:

**230.—BLEACH BATH FOR SUPER-PROPORTIONAL REDUCING**

Water	4 ounces	100 ml.
Mercuric chloride	40 grains	2 grams
Potassium bromide	40 grains	2 grams

The time of the bleaching is so arranged that only in the shadows and the thinner middle tones does bleaching take place. Hence when seen through the back of the negative all the parts that are to be reduced must remain black.

Then the negative is washed well and treated in a

**231.—GOLD CHLORIDE BATH**

Solution of gold chloride 1 : 500

This will have the effect of darkening all the bleached parts and as soon as this happens the bathing is stopped. The negative is now washed and treated with Farmer's reducer until the heavy densities are reduced as required.

With experience this is a very practical and useful method and can provide almost any desired alteration of contrast.

Variations of the method consist in the use of gold or selenium toning of the image, omitting the bleaching bath; in this way the toned parts are protected from the action of the reducer. The bleaching method is, however, safer and allows of better control as the observation of the image during



the bleaching is a certain guide to the progress of the operation. In the gold and selenium toning there is no alteration in image colour, hence there is no observable change to act as a guide to the completeness or otherwise of the reaction.

## INTENSIFICATION

Negatives which are too soft and thin, either through over-exposure, too short development or other mistakes can be improved by intensification. This is called for when it is not possible to produce a satisfactory print by the choice of a suitable hard gradation paper.

There are physical, chemical and optical intensifiers. Chemical intensification is effected by adding something to the silver image—either silver or other compounds. If, for instance, the image is bleached i.e. converted into silver chloride with a solution of ferricyanide and sodium chloride and then redeveloped in a non-staining developer, a moderate increase in density can be achieved. If we use a staining developer, such as pyrogallol, a brown-black image is obtained which has a higher printing density than a neutral black image, provided the positive material is not colour sensitive. This process is called optical intensification, as it depends on the colour of the transmitted light rather than on its intensity. We talk of physical intensification if metallic silver or mercury is deposited on the silver image with the help of a reducing agent in the solution, the silver grains acting as neutral nuclei for this reaction. A suitable solution consists for instance, of silver nitrate, pyrogallol and citric acid, or a mercury salt, metol and citric acid.

Intensifying consists in depositing either metal or a metallic compound of black or dark colour on the silver forming the negative image and so increasing its printing density.

There is one reservation to be made here, and that is the fact that some enlarging papers today are orthochromatic and some panchromatic.\* With such papers a negative having a yellow-brown image such as results from uranium intensification will not give the same result as on a normal, not colour sensitised bromide paper. Hence care should be used in the choice of the method of intensification.

\*See *Enlarging*, by C. I. Jacobson and L. A. Mannheim, Focal Press.

In the following formulae the different types of intensifier are separated according to the degree of density and contrast they can confer on the negative. With the range of printing and enlarging papers available today it will generally be found convenient to use an intensifier of medium type, e.g., mercury, chromium or dyestuff.

It must be emphasised that one can only intensify when there is some image to work on. If under-exposure has been so gross that no image has been developed in the shadows and only clear film exists, then there is nothing to intensify and no use in attempting it.

The action of intensifiers on the negative image is shown on page 349. It will be seen that with almost all intensifiers the denser parts of the image are more strongly intensified than the shadow details, hence the contrast is increased. These are just the properties required, for in the majority of cases our reason for intensifying a negative is to increase density and also to obtain greater contrast.

#### MERCURY INTENSIFIER

This is the most widely used method. The negative must be thoroughly fixed and washed before intensification is attempted. Any trace of hypo left in the negative will cause indelible stains to appear.

The negative is first bleached in the following solution:

##### 232.—BLEACH BATH FOR MERCURY INTENSIFICATION

Mercuric chloride	40 grains	2 grams
Ammonium chloride	40 grains	2 grams
Water	4 ounces	100 ml.

Bleaching must be carried on until all trace of the black silver image has been replaced by a grey-white image.

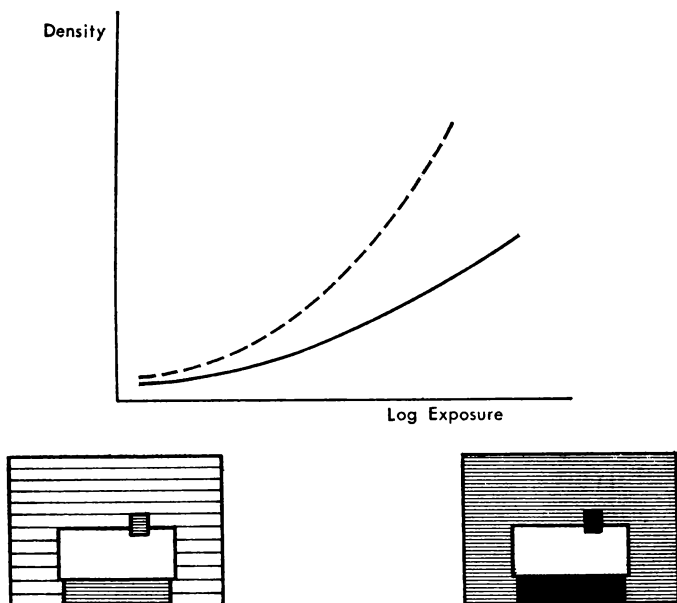
Blackening is carried out after the bleached negative has been given a short wash and may be done with:

##### 233.—BLACKENING BATH FOR MERCURY INTENSIFICATION

- (1) A 10% solution of sodium sulphite or
- (2) A 5% solution of ammonia or
- (3) By using any normal (not fine-grain) developer

Of the three the first gives the least effect and the third

## INTENSIFICATION



Intensification of a weak negative consists in increasing its density by the addition of a black or a dark-coloured layer through chemical action. The additional density is proportionate to the densities already existing in the weak negative. The deep shadows remain virtually unaltered as almost clear emulsion while the highlights attract the greatest proportion of the additional intensity. In this way the contrast of the negative can be increased. The upper part of the diagram shows the effect of intensification on the characteristic curve (full line before intensification and dotted line after intensification). The lower stylised picture shows the effect of the increased contrast.

the most. The second gives an image which does not withstand prolonged light action.

After blackening the negative should be well washed.

A single solution mercury intensifier can be made up:

#### 234.—SINGLE-SOLUTION MERCURY INTENSIFIER

Mercuric chloride	200 grains	10 grams
Ammonium thiocyanate	120 grains	6 grams
Water	4 ounces	100 ml.

Dilute one part with 9 parts of water for use. Maximum intensification requires about 10 minutes. If longer treatment is given the image begins to lose density.

#### MERCURIC IODIDE INTENSIFIER

The following is a simplified method of mercury intensification.

#### 235.—MERCURIC IODIDE INTENSIFIER

To a solution of 120 grains (6 grams) mercuric chloride in 20 ounces (500 ml.) of water add a 10% solution of potassium iodide until the voluminous red precipitate which forms is just re-dissolved. This will require about 3 ounces (75 ml.) of the iodide solution. To the mixture add the following solution:

Sodium sulphite, anhyd.	4 ounces	100 grams
Water to make	20 ounces	500 ml.

If the above intensifier be used alone, the intensified negative has poor keeping properties, it is therefore usual to blacken the image by using any normal developer.

#### URANIUM INTENSIFIER

This method gives strong intensification but the image colour is yellow brown and the keeping properties of the intensified image are not good.

#### 236.—URANIUM INTENSIFIER

A. Water	4 ounces	100 ml.
Uranium nitrate	20 grains	1 gram
Acetic acid glacial	$\frac{1}{2}$ ounce	12.5 ml.
B. Water	4 ounces	100 ml.
Potassium ferricyanide	20 grains	1 gram

For use take one part of A and two parts of B, mix, and then intensify to the required degree. Care must be exercised

in washing the intensified negative, using running water and wash until the water runs smoothly over the intensified surface. If washing be prolonged the density tends to regress. If the yellowish colour of the highlights is objectionable, it can be reduced by treating with a 5% solution of common salt (sodium chloride) in water.

## CHROMIUM INTENSIFICATION

This is a simple, easily controlled, and very satisfactory method which has largely supplanted mercury intensification. A stock solution of potassium dichromate, 10% in strength is used to make up the following baths:

### 237.—CHROMIUM INTENSIFIER

Stock potassium dichromate 10% sol.	$\frac{1}{2}$ ounce	12.5 ml.
Hydrochloric acid conc.	5 minims	0.3 ml.
Water up to	4 ounces	100 ml.

### 238.—ALTERNATIVE CHROMIUM INTENSIFIER

Stock potassium dichromate 10% sol.	$\frac{1}{2}$ ounce	12.5 ml.
Hydrochloric acid conc.	25 minims	1.2 ml.
Water up to	4 ounces	100 ml.

No. 237 gives more intensification than No. 238.

The well washed negative is immersed in the bath until completely bleached; this converts the silver image into a combination of chloride and chromium compound. The negative is now washed until completely free from yellow stain, and developed in daylight, or after exposure to daylight, with a normal developer.

A notable advantage of the method is that if sufficient intensification is not attained in the first attempt the whole treatment can be repeated.

## COPPER-SILVER INTENSIFIER

For very weak negatives M. G. Zelger recommends the following formula:

### 239.—COPPER-SILVER INTENSIFIER

A. Water	20 ounces	500 ml.
Copper sulphate	100 grains	5 grams
Acetic acid glacial	1 ounce	25 ml.
B. Water	10 ounces	250 ml.
Potassium iodide	100 grains	5 grams
Ammonia 880	2 ounces	50 ml.

Two parts of A and one part of B are mixed to form the bleach bath; the negative after bleaching is washed for 15 minutes and blackened in

#### 240.—BLACKENING BATH FOR COPPER-SILVER INTENSIFIER

Water	10 ounces	250 ml.
Silver nitrate	20 grains	1 gram
Sodium acetate	80 grains	4 grams

If desired the film may be hardened after the bleach bath in saturated solution of potash alum.

#### QUINONE-THIOSULPHATE INTENSIFIER

In many cases with high speed photography it is impossible to give adequate exposure. In such cases considerable intensification is the only solution of the problem of getting a printable negative. Sports photographers in particular are always faced with difficulties of this kind, and similar problems are also found in stage and circus photography where the light is poor but reasonably fast shutter speeds are still needed.

Good results are being obtained with the Kodak IN6 quinone-thiosulphate intensifier formula. This is of special value when used on high-speed material, producing a greater effect than any single-solution intensifier.

The intensified image is brownish, and is not indefinitely permanent, being similar in this respect to uranium-toned images. Negatives must be well washed and free from finger marks, and require a preliminary treatment in alkaline formaldehyde hardener, such as Formula 297 on page 406.

#### 241.—KODAK IN6 QUINONE-THIOSULPHATE INTENSIFIER

A.	Warm distilled water	60 ounces	750 ml.
	Sulphuric acid conc.	2 ounces 96 minims	30 ml.
	Potassium dichromate	1 ounce 350 grains	22.5 grams
	Distilled water to make	80 ounces	1000 ml.
B.	Warm distilled water	60 ounces	750 ml.
	Sodium bisulphite	133 grains	3.8 grams
	Hydroquinone	1 ounce 88 grains	15 grams
	Kodak Wetting Agent, 10% solution	1 ounce 270 minims	20 ml.
	Distilled water to make	80 ounces	1000 ml.
C.	Warm distilled water	60 ounces	750 ml.
	Sodium thiosulphate cryst.	1 ounce 350 grains	22.5 grams
	Distilled water to make	80 ounces	1000 ml.

The sulphuric acid must be slowly stirred in.

Distilled water should be used, as a trace of chlorides in the water will greatly reduce the degree of intensification, and may bleach the image.

For use one part of solution A is taken, and two parts of B stirred in, followed by two parts of C. The mixture is well stirred, and another part of solution A is then added. This order of mixing is important, and should not be changed.

After a five minute wash the negatives are hardened by immersing them for about five minutes in the alkaline formaldehyde hardener (No. 297, page 406), and washed again for five minutes in running water. They are then treated in the working solution, made up as described above, for up to ten minutes with continuous agitation. Negatives are best treated singly. They are then well washed, and dried. The working solution should only be made up immediately before it is needed and must be discarded after use.

The brown colour of the image is really an intentional developer stain and is of the same nature as the stain produced on prints when they are put into a fixing bath after development without an intermediate rinse.

The intensified image is destroyed by acid hypo, so intensified negatives must not be placed in fixing solutions, or in washing water contaminated by fixing baths.

The illustrations of defects in negatives on pages 321-336 have been contributed by the *Eastman Kodak Company*, Rochester (U.S.A.), the *Gevaert Factories*, Antwerp (Belgium) and *Ilford Limited*, London.

# *Retouching*

The retouching of negatives today is usually confined to dealing with actual imperfections in the negative or to modifying some excess or want which detracts from the quality of the picture. In earlier days retouching reached such proportions that it was not uncommon to find the finished picture bearing but little resemblance to the original. Such "beautifying" is not the true object of retouching.

## PLAN OF WORK

If retouching is undertaken it should always be carried out in a definite order and according to a deliberate plan.

- (1) The first stage is the wet retouch sometimes called chemical retouching. This comprises the local or partial reduction or intensification of any areas requiring such treatment.
- (2) The treatment of the dried negative comprises dealing with those portions which are too thin and which require blocking out or treating in such a manner as to reduce the amount of light which they can pass.
- (3) If any slip be made in carrying out No. 2, then the matter can usually be remedied by treatment or washing of the negative.
- (4) The next process will be the mechanical reduction of any part of the negative which is too dense, i.e., rubbing down.
- (5) Then will follow, if required, any knife-work, which is used to reduce small local densities, to remove black spots and the like.
- (6) The last retouching to be undertaken is that



carried out with the pencil, and then it is usual to varnish the negative.

This long list does not mean that all or even any of these stages are necessary for every negative. It does mean that if more than one of the operations is required they should follow one another in an ordered sequence so that they do not interfere with one another.

#### PARTIAL REDUCTION OR INTENSIFICATION

In normal reduction and intensification the whole of the negative image is treated, whereas in chemical retouching only certain parts of the image are singled out, as for example in a landscape it may be found that the sky is too dense and hence would print too light.

To partially reduce this portion of the negative the procedure is as follows.

Soak the negative for about 10 minutes to swell the gelatine, and then place it on a white tile, or in a white dish. Take a paint brush, not too full, of Farmer's reducer (see page 342), and distribute the Farmer's reducer carefully over the sky to be reduced. The line where the sky meets the rest of the picture must be carefully traced and not overstepped. Care must be taken not to flood the reducer over the negative. After a few moments the negative should be well rinsed and examined to ensure that action is equal over the desired area. This should be repeated until the necessary amount of reduction has been achieved.

Where very small areas in the negative call for reduction the same procedure can be followed, but a fine camel hair brush should be used to apply the reducing solution. A useful tip is to thicken the reducer with glycerine so that it does not flow so easily and can be more easily confined to the necessary limits.

In special cases those parts of the negative which are not to be reduced may be protected by painting with a waterproof varnish such as shellac. This should be applied, of course, to the dry negative. When the varnish is dry the negative can be treated after swelling in a reducer bath, washed and dried and the protective varnish then removed with benzol or alcohol.

Partial intensification can be carried out by similar means,

using the various intensifiers that are normally used (see page 347).

#### SHADING AND BLOCKING OUT

This is used for those parts of a negative where the image is so thin that it will print too dark, and where local intensification is not possible, or unlikely to give the desired result.

Solutions of red or yellow dyestuffs are used which tint the gelatine of the negative and so retard the passage of light. Such substances are Neo-Coccin, Vanguard yellow, etc.

The art consists in tinting the required part of the negative perfectly evenly. To this end a very pale solution is used to begin with; the brush is well filled and applied firmly and evenly to the negative so that the whole area to be treated is flooded evenly with the dye solution.

With films the dye may be applied to the back of the film, when as in many cases, this carries a gelatine coat. It is not possible to use this method with unbacked 35 mm. (miniature) film for miniature cameras. With glass plates the dye is sometimes applied to the back but causes trouble when enlargements have to be made. When it is desired to use the back of the plate it must first be given a coat of varnish which can be prepared as follows:

#### 242.—MATT VARNISH

Ether	7 ounces	175 ml.
Gum sandarac	$\frac{1}{4}$ ounce	18 grams
Gum mastic	80 grains	4 grams
Benzol	3 ounces	75 ml.

If the ether is quite water free, about 20 minims (1.5 ml.) of water should be added so as to ensure that the varnish will dry with a matt surface.

For dealing with quite small areas which require darkening, fine graphite powder can be used, rubbing it into the matt varnish coating with a leather stumping pencil.

Where there are parts that require a little lightening in cases where the plate has been given a matt varnished back, the varnish can be removed by a knife or by an alcohol damped stump.

In some cases it is necessary to cut out portions of a negative so that they do not print at all. This is usually the

case with unwanted backgrounds, and the usual method is to use an opaque medium, such as Photopake, which is painted either on the face, or more usually on the back of the negative and so cuts out that part of the negative it covers.

Another method is to use the matt varnish and tint it strongly with a red, yellow or other dye so that no actinic light can pass. Such dyes as congo red, quinoline yellow, malachite green, etc., are used for this purpose, but the process is only suitable for use with glass negatives from which contact copies are required.

### SPOTTING

Spotting is the name given to the operation of removing or filling in small spots, flecks or pin holes in the negative. The procedure naturally depends on the nature of the spot.

Whatever the type of spot the aim is to treat it so that it is hidden, hence if it be a pin hole in a light part of the negative, it is spotted out by using special water-colour paint and a very fine pointed brush. The first step is to ensure that the tint used is the same shade as that part of the negative where the spot occurs. This is achieved by a trial or two on a piece of white paper. Then the spot or pin hole is carefully touched with the point of the brush, laden with the retouching medium, until the required density is built up. Photopake is sometimes used, but the water colour retouching medium is preferable as Photopake on a thinly covered part of the negative tends to give a light coloured spot or area on prints.

Some workers prefer to do their retouching on the print and not on the negative, but it is obvious that if many prints are to be made the retouching should take place on the negative before printing.

### DRY REDUCTION

Reducing normally depends upon chemical action, that is the solution of part of the silver image, but local reduction can be carried out by mechanical means, that is by rubbing down or abrading the heavier parts of the image. Globe metal polish has long been used for this purpose, but if unobtainable a substitute may be prepared as follows:

#### 243.—DRY REDUCER

Paraffin wax	1 ounce	25 grams
Tallow	1½ ounces	36 grams
Vaseline	4 ounces	100 grams
Oleic acid	2½ ounces	65 grams
Nitrobenzene	15 minims	1 ml.

This mixture is melted at as low a temperature as possible and stirred until thoroughly mixed. Then there is added with careful stirring and mixing while warm,

Tripoli (Finest Kieselguhr)	10 ounces	250 grams
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The tripoli may be replaced by very finely powdered pumice which has been sifted through fine silk bolting cloth. Or the pumice powder may be used dry or with the following medium:

#### 244.—ALTERNATIVE DRY REDUCER MEDIUM

Oil of turpentine	2 ounces	50 grams
Benzene or carbon tetrachloride	2 ounces	50 grams

The application of the abrasive may be made with the aid of artist's stumps, either of leather or paper, or by using a pen holder, the rounded end of which has been covered with linen or wash leather, or for very small areas chisel shaped, pear or other similar wood tools.

When the reduction is complete every trace of the abrasive material must be carefully removed with brush and alcohol or benzol.

#### KNIFING

This is normally a more drastic method of retouching than the use of abrasive, for it allows of the complete removal of part of the image if desired. The retouching knife must have a razor edge and the edge must be constantly renewed by the proper use of an oilstone.

Knifing is carried out by making parallel strokes one after the other until the whole area to be reduced has been covered. The process is now repeated with the direction of the strokes at a decided angle to the first set and so on. In this way if the work is carefully done the individual strokes are quite imperceptible.

With negatives which have already been reduced with

Farmer's reducer the knife sometimes takes badly; in such a case the area can be lightly rubbed down with Globe metal polish or similar very lightly abrasive pastes.

## PENCIL RETOUCHING

The art of pencil retouching can easily be abused, and its excessive use has brought discredit on certain branches of photography in past times. Used with discretion, that is not for the beautification of a picture but for the correction of blemishes or errors, it can perform valuable service.

In order that the negative will take the pencil properly, it is usually necessary to treat it with a varnish. Certain portrait plates and films are actually supplied with a matt surface to facilitate retouching, but in the absence of this a matt varnish must be used.

## VARNISHING

One of the most useful is the water varnish made up as follows:

### 245.—WATER VARNISH

Orange shellac	1½ ounces	36 grams
Borax	200 grains	10 grams
Carbonate of soda	40 grains	2 grams
Glycerine	40 minims	2 ml.
Water	16 ounces	400 ml.

The borax and soda are dissolved first in about half the water, the solution warmed and the shellac added and stirred until dissolved, which will probably require gentle heating. Then filter through clean linen and make up to the full quantity after adding the glycerine.

The negative can be bathed in this varnish and so given a matt coat, both back and front, which will easily take retouching.

Some workers prefer a warm alcohol varnish and a useful one is:

### 246.—ALCOHOL VARNISH

Bleached shellac (powdered)	8 ounces	200 grams
Gum sandarac	2 ounces	50 grams
Gum mastic	¼ ounce	6 grams
Gum dammar	¼ ounce	6 grams
Castor oil	5 drops	5 drops
95% alcohol	80 ounces	2000 ml.

When the shellac and the gums are completely dissolved the varnish must be filtered. Before it is used the plate must be warmed and sufficient of the varnish poured on to flow evenly over the surface to be matted, the excess being allowed to flow back into the varnish bottle from a corner of the plate.

This matt coating can be removed, if necessary, by dissolving off with alcohol.

A cold varnish can also be used, namely:

#### 247.—COLD VARNISH

Gum dammar	$\frac{1}{2}$ ounce	6 grams
Carbon tetrachloride	4 ounces	100 ml.
When dissolved add manilla copal	$\frac{1}{2}$ ounce	6 grams

Solution takes some time and is best helped by heating the mixture in a water bath. The varnish should be filtered hot. Note that it is not inflammable.

Another cold varnish is prepared by taking:

#### 248.—ALTERNATIVE COLD VARNISH

Gum sandarac	2 ounces	50 grams
Benzene	8 ounces	200 ml.
Acetone	10 ounces	250 ml.
Alcohol 95%	4 ounces	100 ml.

Solution can be aided by careful warming in a water bath and the varnish must be filtered warm. The cold varnishes can be applied to well dried negatives without their being warmed.

The cold varnishes give a somewhat thinner film than the warm varnish, but permit of an even heavier retouching being carried out.

Another type of matting is that which is applied with a wad of linen and not poured over the negative. These varnishes have the advantage that they dry very rapidly but are not particularly suitable for use on negatives which are to be enlarged.

#### 249.—NORMAL MATTING VARNISH

Gum dammar	1 ounce	25 grams
Oil of turpentine	5 ounces	125 ml.

#### 250.—RAPID MATTING VARNISH

Gum dammar	$\frac{1}{2}$ ounce	12 grams
Oil of turpentine	3 ounces	75 grams
Petrol-ether	3 ounces	75 grams
Oil of lavender	30 minims	2 grams

These two varnishes give a very thin matt coating which will only take very light retouching.

When negatives are intended for enlarging the varnish must be applied equally over the whole of the negative surface but, for contact prints only, the varnish can be applied just where retouching is required.

In addition to providing a surface which takes retouching in a satisfactory manner, these varnishes also act as a protective coating to the negative and preserve it from scratches or other change.

A simple protective varnish can be prepared from waste film which has been cleansed free from all gelatine coating and carefully dried.

#### 251.—CELLULOID VARNISH

Celluloid	$\frac{1}{2}$ ounce	6 grams
Amyl acetate	4 ounces	100 ml.
Acetone	4 ounces	100 ml.

#### APPLYING THE VARNISH

For good results to be obtained it is important that varnish be applied so that an even coat covers the whole of the negative. The negative is first dusted carefully with a soft brush, and a small pool of the varnish poured on to the centre of the plate. By tilting the plate carefully, first one way and then another, the varnish is caused to flow evenly over the whole surface. Finally, the plate is tilted so that the excess varnish flows back into the varnish bottle from the right lower corner.

To varnish film negative they are first fastened down to a glass plate with a suitable cement and the process then carried out as for a glass plate. Note that shellac or gum dammar varnishes may be used with films, but the celluloid varnish must not be used as it would attack the film base.

#### PENCILS FOR RETOUCHING

Pencils of varying hardness are used in retouching. Soft pencils give dark marking and density, while harder pencils give lighter effects. As a general rule the pencil chosen for a particular piece of work should need to go over the area 4-5 times in order to build up the necessary density. The pencil

is used to give a stippling effect on the film, and both practice and good judgment are required for success.

If, by chance, too heavy a retouch has been given, correction can be achieved by removing the blackening with benzine or turpentine and the area dealt with again.

All retouching work should be carried out on some form of retouching desk. This consists essentially of a frame (page 329), which encloses a ground glass sheet upon which the negative is laid. The frame can be set at any convenient angle and light from a window or other light source is reflected by a mirror through the ground glass screen. If artificial light is used, the mirror should be covered by a white card or sheet of paper to diffuse the light.



## Processing Colour Films

Practically all modern colour films rely on the formation of dye images in three separate emulsion layers by a process of chromogenic development similar to that described on page 223. Before giving details of processing procedures for colour films it is advantageous to outline the basic principles upon which modern colour films are based.

Modern colour materials utilise the *subtractive* principle of colour reproduction which is the reproduction of colours by the formation of various amounts of *cyan*, *magenta*, and *yellow* dyes in three separate red, green and blue sensitive emulsion layers. Cyan, magenta and yellow are the *subtractive primaries* and are equivalent to minus red minus green, and minus blue respectively:

Minus red  $\equiv$  cyan (blue + green)

Minus green  $\equiv$  magenta (blue + red)

Minus blue  $\equiv$  yellow (green + red)

The diagrams on page 365 show these subtractive primaries together with the composition of white light and the *additive primaries* (red, green and blue).

The subtractive primaries are used in modern colour material because they possess the property that they can be superimposed in all possible combinations to form an infinite range of colours, whereas the additive primaries do not have this property (see page 366). Thus:

Red  $\equiv$  magenta + yellow (white minus green and minus blue)

Green  $\equiv$  cyan + yellow (white minus red and minus blue)

Blue  $\equiv$  cyan + magenta (white minus red and minus green)

Most modern colour photographic materials are in the form of an *integral tripack* (see diagram on page 367) which consists of a blue sensitive layer that records the blue portions of the original scene as a yellow image, a green sensitive layer that records the green portions of the original scene as a

magenta image, and a red sensitive layer that records the red portions of the original scene as a cyan image. Integral tripacks also contain a yellow filter layer immediately below the top blue sensitive layer to filter out blue light to which the green and red sensitive layers are also slightly sensitive. The procedure described above and illustrated on page 367 results in the formation of a colour negative, because the colours in the negative are complementary to those of the original scene. It can be worked out from the various colour equations given previously that if a colour negative is printed on to a similar tripack material coated on paper a positive print will be formed: e.g. consider the reproduction of a red: this will be recorded in the negative as a cyan (blue + green) image which on printing will expose the blue and green sensitive layers of the paper to form yellow and magenta images (minus blue and minus green, i.e. red).

Reversal processing, however leads directly to a positive transparency as shown in the diagram on page 368.

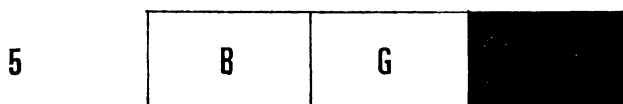
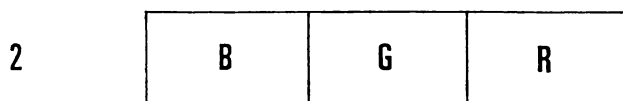
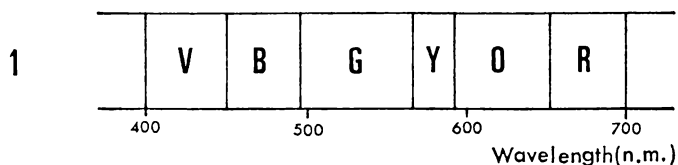
With negative colour films, the processing is comparatively simple and can be carried out with the same equipment as for black and white materials. Colour processing, however, requires much stricter control of processing conditions than black and white processing. Development temperature must be maintained within very close limits ( $\pm\frac{1}{4}^{\circ}\text{C}.$ ), pH values of the processing solutions must be kept within the specified values and development times must not be altered from those recommended by the manufacturer.

The processing of reversal colour film requires more steps leading to a positive transparency. The procedure is straightforward and can also be carried out with the same equipment as used for black-and-white material. The main points to watch are also temperatures and times, and the instructions given by the manufacturers must be carefully followed.

#### “OFFICIAL” AND “SUBSTITUTE” FORMULAE

Amateurs who prefer to make up their own solutions will find this a straightforward job in black-and-white photography. There is no doubt as to the choice of the formula as all manufacturers have published the most suitable formulae for their products. Besides, in nearly all cases it is possible to use universal formulae suitable for a wide range of makes of film.

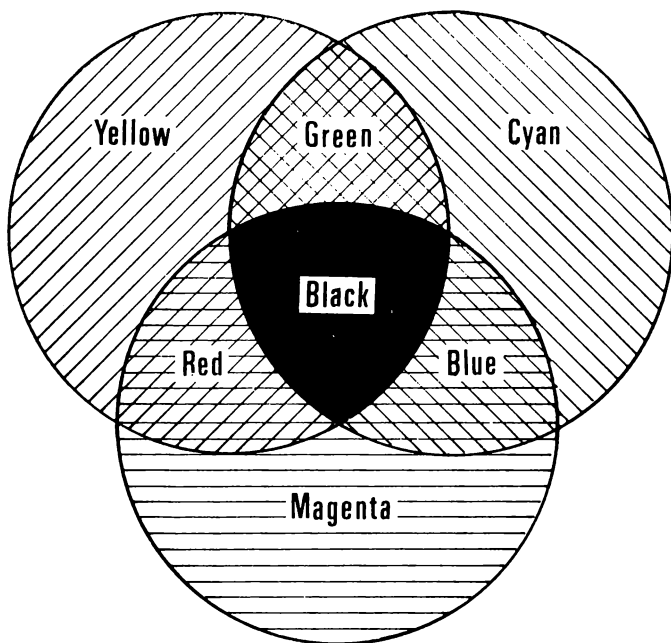
## WHITE LIGHT, THE ADDITIVE AND SUBTRACTIVE PRIMARIES



V=Violet B=Blue G=Green Y=Yellow O=Orange  
R=Red

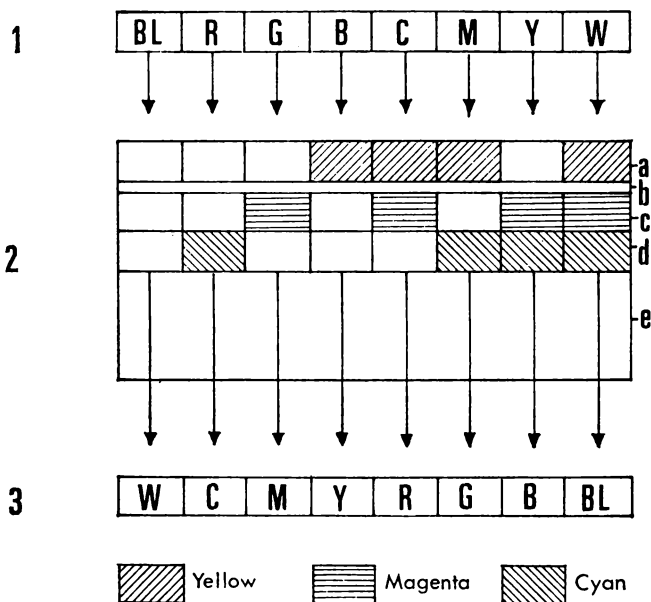
- 1: The approximate distribution of colours in the visible spectrum.
- 2: The visible spectrum can be divided into three equal regions of blue, green and red known as the *additive primaries*.
- 3-5: Subtracting each additive primary colour in turn from the visible spectrum gives the *subtractive primaries*. Thus: minus blue appears *yellow* (3), minus green appears *magenta* (4), and minus red appears *cyan* (5).

## SUBTRACTIVE COLOUR SYNTHESIS



The above diagram shows that superimposition of the subtractive primaries) yellow, magenta, and cyan) can form red, green, blue, and black.

## FORMATION AND APPEARANCE OF A COLOUR NEGATIVE



1: The original, consisting of areas of black (BL), red (R), green (G), blue (B), cyan (C), magenta (M), yellow (Y), and white (W).

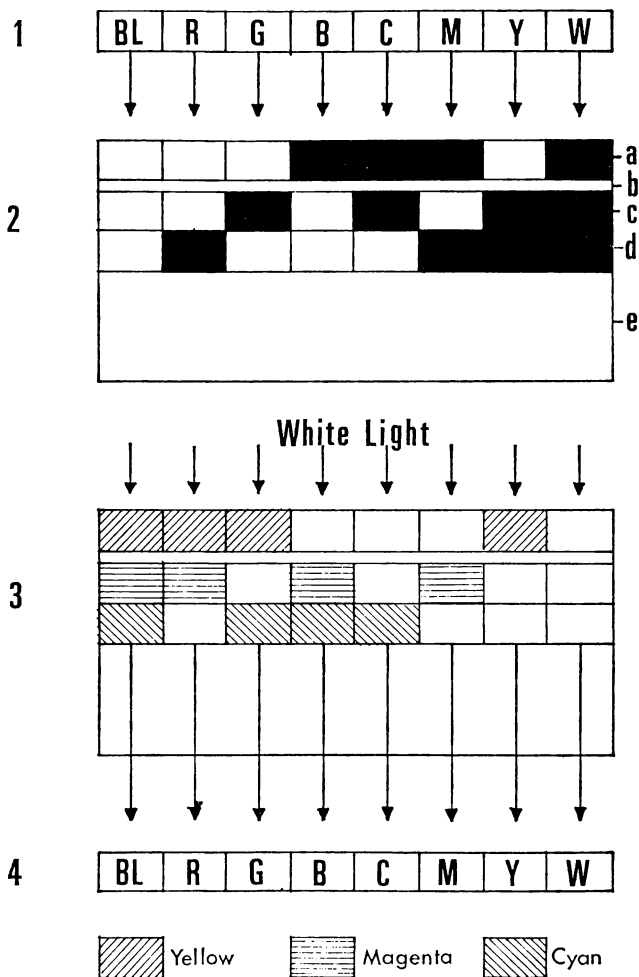
2: The integral tripack negative material consisting of: a blue sensitive layer (a) containing a yellow coupler, a yellow filter layer (b), a green sensitive layer (c) containing a magenta coupler, and a red sensitive layer (d) containing a cyan coupler, coated on a film base (e).

The yellow filter layer (b) is present to filter out blue light to which the red and green layers (c and d) are also slightly sensitive.

The shaded portions represent the formation of dyes in the appropriate layers after exposure, colour development and removal of the silver images.

3: The appearance of the negative which is complementary in both hue and tone to the original. Colour negatives generally have an orange cast which is the colour of the mask used to correct for dye imperfections and ultimately lead to more faithful colour reproduction at the printing stage.

## FORMATION AND APPEARANCE OF A COLOUR POSITIVE TRANSPARENCY



- 1: The original.
  - 2: The integral tripack after exposure and the first black and white development stage.
  - 3: The integral tripack after the colour development stage and removal of the silver image.
  - 4: The appearance of the colour transparency.
- Explanations of the symbols used in the above diagram can be found on p.367.

In colour photography, the situation is rather different. First, only a few manufacturers have published processing formulae; most recommend the use of the chemicals packed by them or the return of the films to them or other processing stations. Secondly, colour materials of various makes are so different in their characteristics that universal formulae can be used only to a very limited extent.

These facts have to be borne in mind when using the information published in this chapter. Formulae which have been officially published by the manufacturer are marked as such. In most cases, however, the reader will have to make use of "substitute" formulae as published by various experts or by the author. The majority given here are those formulated by E. Gehret and are published in the *British Journal of Photography Annual*.

Colour processing with independent formulae is thus more in the nature of an experiment than a standardised technique. Excellent results can be obtained provided that the job is tackled systematically and adjustments to the suggested procedure are made when necessary.

#### COLOUR NEGATIVE FILM

The first step in processing colour negative film is colour development. This produces a dyestuff image together with a silver image in each layer.

Then follows an intermediate step to stop development and remove developer and by-products. This can be done simply by prolonged washing, but a definite after-development effect takes place during washing. In some processes this effect is made use of to complete development, mainly in the bottom layers of the film, and to get a good colour balance. If a stop-bath is used, the development is interrupted immediately, and the removal of certain by-products becomes easier. The washing time can therefore be reduced. In other processes a combined stop-fix bath is used, usually with a hardening agent.

The first cumulative stage of the processing procedure, i.e. the production of the colour "picture" by the developer and subsequent operation—stop bath and/or wash—must be considered as a sequence specific to individual makes and cannot be replaced by any sort of universal treatment.

The next operation is the removal of the unwanted silver image (and the unchanged silver halide, if no fixing agent has been used in the stop-bath). The traditional method is to use a potassium ferricyanide bleach bath followed by a fixing bath. An alternative is a combined bleach-fix solution in which the ferricyanide is replaced by organic iron compounds. Bleach-fix solutions of this type have good keeping properties and less tendency to stain than ferricyanide solutions. The processing is finished as usual by a thorough wash.

It is not possible to use one and the same formula for all types and makes of colour film. Better results can be obtained by adapting the formula to the film as suggested later on. The other stages of the process are less critical and it is possible to use universal formulae for different makes of colour film.

#### COLOUR DEVELOPMENT

The most usual developing agents are salts of diethyl-p-phenylenediamine (4-amino-N,N-diethylaniline) or derivatives. There is quite a choice of agents of these types:

#### LIX.—COLOUR DEVELOPING AGENTS

<i>Chemical Names</i>	<i>Trade Names</i>
Diethyl-p-phenylenediamine sulphite N,N-Diethyl-p-phenylenediamine sulphite p-Diethylaminoaniline sulphite 4-Amino-N,N-diethylaniline sulphite	Genochrome (May & Baker)
Names as above but hydrochloride	CD1 (Kodak)
Ethylhydroxyethyl-p-phenylenediamine sulphate N-Ethyl-N-hydroxyethyl-p-phenylenediamine sulphate p-Ethylhydroxyethylaminoaniline sulphate 4-Amino-N-ethyl-N-( $\beta$ -hydroxyethyl)aniline sulphate	Droxychrome (May & Baker)
N,N-Diethyl-3-methyl-p-phenylenediamine hydrochloride 2-Amino-5-diethylaminotoluene hydrochloride 4-Diethylamino-o-toluidine hydrochloride 4-Amino-N,N-diethyl-3-methylaniline hydrochloride	Tolochrome (May & Baker)  CD2 (Kodak)
N-Ethyl-3-methyl-N-( $\beta$ -methylsulphonamidoethyl)-p-phenylenediamine, sesquisulphate 4-Amino-N-ethyl-N-( $\beta$ -methylsulphonamidoethyl)-m-toluidine, sesquisulphate 4-Amino-N-ethyl-3-methyl-N-( $\beta$ -methylsulphonamidoethyl)aniline sesquisulphate	Mydochrome (May & Baker)  CD3 (Kodak)
N-ethyl-N-( $\beta$ -hydroxyethyl)-3-methyl-p-phenylenediamine sulphate 4-amino-3-methyl-N-ethyl-N-( $\beta$ -hydroxyethyl)aniline sulphate	CD4 (Kodak)



On no account should the above chemicals be allowed to come in contact with the skin or inhaled.

In addition to one of these agents the colour developer contains a large amount of alkali, such as potassium carbonate and usually a small amount of sodium sulphite to improve keeping properties. Further ingredients are hydroxylamine hydrochloride as an anti-stain agent, potassium bromide or iodide as an anti-fogging agent, and calgon as water softener.

**LX.—COLOUR NEGATIVE DEVELOPERS\***

	252 <i>Kodak C-22</i>	253 <i>Agfa</i>	254 <i>Kodak C-41</i>
Benzyl alcohol	5	—	—
Calgon, sodium hexameta- phosphate or tripolyphosphate	2	2	2
Sodium metaborate, cryst.	85	—	—
Hydroxylamine sulphate	—	1.4	3
Sodium sulphite, anhyd.	2	2	2
Sodium or potassium bisulphate	—	—	7
Sodium bicarbonate	—	—	8
Potassium carbonate, anhyd.	—	75	30
Potassium bromide	1.6	2.5	1.8
6-Nitrobenzimidazole 0.3% solution	—	—	10
CD3	5.3	—	—
CD4	—	—	3.2
4-Amino-N,N-diethylaniline sulphate	—	2.8	—
Water to pH	1000 10.6-10.7	1000 11.0-11.3	1000 10.1-10.2

\*These substitute formulae are those published in the *British Journal of Photography Annual* (1977). See also notes on page 375.

**Notes:** It is best to make up the stock solution containing all the ingredients, except the developing agent, in slightly less than 1000 ml. and shortly before use add the developing agent and make up to 1000 ml. The developing agent of Formula 253 tends to form oily droplets when added to the remainder of the developer. It is recommended that this developing agent be dissolved in 20 ml. of water prior to its addition to the developer with constant stirring.

**STOP-BATH**

As in black-and-white processing the stop-bath for negative colour film is a weakly acid solution, but the pH value must

be more carefully adjusted and controlled. The acid is usually acetic acid sometimes with addition of sodium acetate to increase the pH value to between pH 5.0 and 6.0. As mentioned above, in some cases an addition of fixing and hardening agents is recommended and Tables LIII and LXV list a number of such variations of stop-bath formulae. Formula 255 is a typical stop-bath recommended by E. Gehret for Kodak colour negative films.

**255.—STOP-BATH FOR COLOUR NEGATIVE FILMS (E. GEHRET)**

Glacial acetic acid	20 ml.
Sodium sulphite, anhyd.	10 grams
Water to	1000 ml.
pH	4.3-4.7

**256.—INTERMEDIATE BATH FOR AGFA COLOUR NEGATIVE FILMS**

Magnesium sulphate, cryst.	30 grams
Colour developer (Formula 253)	30 ml.
Water to	1000 ml.
pH	10.2-10.5

**HARDENING-BATH**

After development has been stopped it is normal procedure to use a hardening-bath to reduce the possibility of damage to the emulsion during subsequent processing stages. A typical hardening-bath based on formalin is as follows:

**257.—HARDENER FOR COLOUR NEGATIVE FILMS (E. GEHRET)**

Formalin	20 ml.
Sodium carbonate, anhyd.	10 grams
Water to	1000 ml.
pH	10.4-10.8

**BLEACH- AND FIXING-BATHS**

Generally potassium ferricyanide or iron sequestrane is used together with bromide and various pH controlling agents as a bleach-bath (see Table LXI) followed by fixing in sodium or ammonium thiosulphate (Table LXII). The main function of the bleach solution is to convert the silver image, formed together with the dye image in colour development, to silver bromide which can be removed by fixing.

# LXI.—BLEACH-BATHS FOR COLOUR NEGATIVE FILMS\*

	258 <i>Kodak C-22</i>	259 <i>Agfa</i>	260 <i>Kodak C-41</i>
Potassium nitrate, cryst.	25	—	—
Irons sequestrene (Ciba-Geigy)	—	—	100
Potassium ferrocyanide	—	5	—
Potassium ferricyanide	20	20	—
Potassium bromide	8	12	50
Boric acid	5	—	—
Borax, cryst.	1	—	—
Monosodium phosphate, cryst.	—	0.9	—
Disodium phosphate, cryst.	—	2.7	—
Ammonia, 20% solution	—	—	6
Water to	1000	1000	1000
pH	6.6-7.0	5.8-6.2	5.9-6.1

# LXII.—FIXING BATHS FOR COLOUR NEGATIVE FILMS\*

	261 <i>Kodak C-22</i>	262 <i>Agfa</i>	263 <i>Kodak C-41</i>
Ammonium thiosulphate	120	—	120
Sodium thiosulphate, cryst.	—	200	—
Potassium metabisulphite	20	—	20
Sodium sulphite, anhyd.	—	10	20
Water to	1000	1000	1000
pH	4.4-4.6	8.0-9.0	5.8-6.5

\*British Journal of Photography Annual (1977).  
See also notes on page 375.

The pH value of the bleach-bath is critical for Agfacolor CNS films because mask formation for the cyan layer occurs in this bath unlike Kodak and 3M colour negative materials in which masking occurs in the development stage. Kodak and 3M materials use coloured couplers, i.e. the mask is already present and is destroyed where colour development takes place.

Combined bleach-fix solutions simplify the process but such solutions prepared by mixing hypo with ferricyanide (Farmer's reducer, Formula 220) have very limited keeping properties. One method of making up a bleach-fix solution is based on the use of iron-EDTA (ethylenediaminetetracetic acid) complex with hypo. Two typical bleach-fix formulae are:

#### 264.—BLEACH-FIX BATH (G. THEILGAARD)

Sodium hydroxide	23.5 grams
Ethylenediaminetetraacetic acid	42 grams
Ferric chloride, cryst.	26 grams
Hypo cryst.	160 grams
Sodium sulphate, anhyd.	15 grams
Water to make	1000 ml.
pH	7.0

#### 265.—RAC RAPID BLEACH-FIX (M. LEVY and H. A. WILLEY)

Ammonium thiosulphate	100 grams
Sodium sulphite, anhyd.	7 grams
Iron sequestrene, Geigy NaFe 13%	100 grams
Water to make	1000 ml.
pH	5.9

The rapid bleach-fix solution (265) may be advantageously used to replace all processing steps following development for those negative films normally processed in the Kodak C-22 and C-41 processes. The time of treatment is 3 minutes in the bleach-fix followed by a wash for 2 minutes and then a rinse in wetting agent for  $\frac{1}{4}$  minute. Thus the total processing time for C-22 processed materials is reduced from 52 minutes (see Table LXIII) to  $18\frac{1}{4}$  minutes with the added convenience of using only two processing solutions.

### COLOUR REVERSAL PROCESSING

The steps in processing a reversal colour film are:

The film is first developed in a black/white negative developer producing a negative silver image. After several intermediate steps such as treatment in stop and hardening solutions, the unaffected silver salts are re-exposed to a strong light source. Then follows colour development where the re-exposed silver salts are reduced to silver, and dyes are simultaneously produced in the three layers. There may again follow intermediate treatment in hardening and stop solutions, and in the next step all the silver is removed, leaving only the dyes and silver halide which is dissolved in the usual way with a hypo solution. The majority of the formulae in this section are those devised by E. Gehret and are given in the British Journal of Photography Annual 1977.

### FIRST DEVELOPMENT

The choice of the first developer for reversal films depends on the make of the film: there is no universal formula.

**LXIII.—COLOUR NEGATIVE PROCESSING PROCEDURES**  
*Processing Steps and Formulae (Brit. J. Phot. Annual 1977)*

	Kodak C-22	Agfa	Kodak C-41
1. Colour Developer	No. 252, 13 min., $24 \pm 0.3^\circ\text{C}$ .	No. 253, 8 min., $20 \pm 0.2^\circ\text{C}$ .	No. 254, 3 min. 15 sec. $37.8 \pm 0.15^\circ\text{C}$ .
2. Intermediate or Stop-Bath	No. 255, 4 min., $20-24^\circ\text{C}$ .	No. 256, 4 min., $20 \pm 0.2^\circ\text{C}$ .	—
3. Hardener	No. 257, 4 min., $20-24^\circ\text{C}$ .	—	—
4. Wash	4 min., $20-24^\circ\text{C}$ .	15 min., $14-20^\circ\text{C}$ .	—
5. Bleach	No. 258, 6 min., $20-24^\circ\text{C}$ .	No. 259, 5 min., $20 \pm 0.5^\circ\text{C}$ .	No. 260, 4 min. 20 sec. $38 \pm 3.0^\circ\text{C}$ .
6. Wash	4 min., $20-24^\circ\text{C}$ .	5 min., $14-20^\circ\text{C}$ .	1 min. 05 sec. $38 \pm 3.0^\circ\text{C}$ .
7. Fix	No. 261, 8 min., $20-24^\circ\text{C}$ .	No. 262, 5 min., $18-20^\circ\text{C}$ .	No. 263, 4 min. 20 sec. $38 \pm 3.0^\circ\text{C}$ .
8. Final Wash	8 min., $20-24^\circ\text{C}$ .	10 min., $14-20^\circ\text{C}$ .	3 min. 15 sec. $38 \pm 3.0^\circ\text{C}$ .
9. Wetting Agent	† min., $20-24^\circ\text{C}$ .	$\frac{1}{2}$ min., $14-20^\circ\text{C}$ .	1 min. 05 sec. $24^\circ\text{C}$ .
10. Drying	Max. $49^\circ\text{C}$ .		Max. $43^\circ\text{C}$ .

*Notes:*

1. The now obsolete Kodak C-22 substitute process was appropriate for processing Kodacolor-X, Ektacolor Professional L and S, Cilcolor, Fujicolor N 100 and NK, GAF (Ansco) Color Print, Sakuracolor N 100, and 3M Color Print.

2. The Agfa substitute process is claimed to be appropriate for processing Agfacolor CN 17, Universal, CNS, CNS/2 (CNS Pocket Special) 80S, and Perucolor.

3. The Kodak C-41 substitute process is claimed to be appropriate for processing Kodacolor II, Vericolor II, Fujicolor II, Sakuracolor II, Turacolor, and 3M Color Print (New).

4. The recommended agitation procedure for both the C-22 and Agfa substitute processes is continuous agitation for the first 15 seconds followed by agitation for 5 seconds every  $\frac{1}{2}$  minute.

5. For the C-41 substitute process the following procedures are recommended for agitation and maintaining the temperature: (a) prepare a water bath at  $41^\circ\text{C}$ . and bring the solutions

up to 38°C. (b) Fill the developing tank with developer and agitate continuously for 20 seconds, then immerse the tank in the water bath to just below the top of the lid. (c) Remove the tank from the water bath and agitate for 5 seconds then replace in water bath. (d) Repeat giving 6 agitations per minute. (e) After draining the developer from the tank (allow 10 seconds) repeat this agitation procedure in the bleach. (f) In this process the wetting agent solution should also contain formalin. A suitable formula is No. 293.

#### LXIV.—FIRST DEVELOPERS FOR COLOUR REVERSAL PROCESSES\*

	266 <i>Kodak</i> E3**	267 <i>Kodak</i> E4	268 <i>Agfa</i> - chrome
Calgon, sodium hexametaphosphate or tripolyphosphate	—	2	2
Metol	6	6	3
Sodium sulphite, anhyd.	40	50	40
Phenidone	—	—	—
Hydroquinone	6	6	6
Borax, cryst.	—	—	—
Sodium metaborate, cryst.	—	—	—
Sodium carbonate, anhyd.	40	30	50
Trisodium phosphate, cryst.	—	—	—
Potassium bromide	2	2	2
Sodium thiocyanate	2	1.3	1.8
Sodium hydroxide	—	2	—
Potassium iodide, 0.1% solution	—	6	6
6-Nitrobenzimidazole nitrate 0.2% solution	15	—	—
Water to	1000	1000	1000
pH	9.9-10.0	10.1-10.3	10.1-10.3

\*Substitute formulae from British Journal of Photography Annual (1977).

\*\*The obsolete E3 process is included for comparison.

Certain features are, however, common to these developers. First, they all possess a very high development energy and are used more concentrated than for normal black-and-white development. They also contain more alkali.

Secondly, the M.Q. types contain a low concentration of thiocyanate which dissolves silver halide and it therefore helps to produce transparencies with clear whites by removing any excess of silver halide. Most of these developers are of the M.Q. type.

The M.Q. developers require either an efficient stop or a combined stop-hardening bath (Table LXV) after development and then a short wash.

Phenidone (0.5 grams) may be used in place of metol in the Kodak E3 Formula 266.

Because of the high temperatures (29°C.) and high pH values used in the Kodak Ektachrome E4 process (Formula 267) a pre-hardening bath is required together with a neutraliser before the first development is started:

**269.—PRE-HARDENER FOR EKTACHROME E4 PROCESS**  
(E. GEHRET)

Nitrobenzimidazole nitrate	0.03 gram
Sodium or potassium bisulphate	0.8 gram
2,5-Dimethoxytetrahydrofuran	5 ml.
Sodium sulphate, anhyd.	136 grams
Formalin	30 ml.
Potassium bromide	3 grams
Water to	1000 ml.
pH	4.9-5.0

*Note:* 2,5-Dimethoxytetrahydrofuran is readily absorbed by the skin and has a harmful vapour. This compound should be used in a well-ventilated room and contact with the liquid should be avoided.

**270.—NEUTRALISER FOR EKTACHROME E4 PROCESS**  
(E. GEHRET)

Hydroxylamine sulphate	20 grams
Glacial acetic acid	10 ml.
Sodium acetate, cryst.	24 grams
Potassium bromide	16 grams
Sodium sulphate, anhyd.	25 grams
Potassium metabisulphite	5 grams
Sodium hydroxide	6 grams
Water to	1000 ml.
pH	5.1-5.2

**COLOUR DEVELOPMENT**

Before the film can be colour developed, it has to be re-exposed. This is usually carried out at a distance of about 3 feet from a Photoflood lamp for 3 minutes, 1½ minutes on each side. The film must be completely re-exposed.

The Kodak E4 process uses a colour developer that contains a chemical fogging agent (t-butylaminoborane) and requires no re-exposing. This compound is, however, *extremely toxic* and all contact and inhalation of the vapour must be avoided. In the substitute formulae given here (No. 275) t-butylaminoborane may be omitted provided that the film is re-exposed to white light in the normal manner.

The composition of the colour re-developer is similar to the formulae for negative film (pages 223-226), but in most cases a colour developer of higher energy is used, i.e. developers containing an alkali hydroxide or a tri-alkali phosphate or a so-called "accelerator". Some of the colour developer formulae given (Table LXVI) also contain: citrazinic acid (2,5-dihydroxy-*iso*-nicotinic acid) to prevent excessive contrast of the dye image, EDTA (ethylenediaminetetracetic acid) as an accelerator, benzyl alcohol to aid diffusion of the developing agent or its oxidation products to the site of coupling, and the usual restrainers and antifoggants. The time of colour development is generally 10-20 minutes.

**LXV.—STOP AND HARDENING BATHS FOR COLOUR REVERSAL PROCESSES\***

	271 Kodak E3	272 Kodak E4	273 Agfa- chrome
Sodium acetate, cryst.	—	5.3	40
Glacial acetic acid	—	30	10
Potassium alum	—	—	—
Chrome alum	30	—	—
Sodium or potassium bisulphate	—	—	—
Potassium metabisulphite	—	—	—
Boric acid	—	—	—
Water to	1000	1000	1000
pH	3.3-3.7	3.4-3.6	5.0-5.4

\*British Journal of Photography (1977).

In all cases it is necessary to put the film after development through stop and hardening baths or combined solutions (Table LXV) and it must then be thoroughly washed.

The removal of silver is carried out in bleaching solutions containing potassium ferricyanide, in most cases in mixture with potassium bromide (Table LXVII). These solutions convert the black metallic silver produced in the first developer as well as in the colour developer into silver bromide which is then removed by a 20% solution of hypo (see Table LXVIII). A final wash of about 20 minutes finishes the process.

The formulae for bleach- and fixing-baths given in Tables LXVII and LXVIII are those that have been found to work best for the particular type of film being processed. For reversal

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1 kg = 1/2. 96.



processing the steps following colour development are less critical than those in colour negative processing and some interchangeability of these solutions is possible as the main requirement is that the removal of silver and unchanged silver halides is complete. Care should be exercised in interchanging some solutions (see page 380). It is always advisable to run tests prior to an important processing run.

# **LXVI.—COLOUR DEVELOPERS FOR REVERSAL PROCESSING\***

	274 Kodak E3	275 Kodak E4	276 Agfa- chrome
Sodium sulphate, anhyd.	—	—	—
Sodium metaborate, cryst.	—	—	—
Calgon, sodium hexametaphosphate or tripolyphosphate	—	2	2
Trisodium phosphate, cryst.	40	40	—
Sodium carbonate, anhyd.	—	—	—
Sodium hydroxide	5.6	5	—
Potassium carbonate, anhyd.	—	—	80
Ethylenediamine sulphate	8	7.6	—
Benzyl alcohol	5	10**	—
t-butylaminoborane	—	0.1	—
Citrazinic acid	1.3	1.3	—
Hydroxylamine hydrochloride	—	—	2.2
EDTA tetrasodium	—	3	—
$\beta$ -Phenylethylamine	—	—	3
Sodium sulphite, anhyd.	—	5	2
Potassium bromide	—	1	1
Potassium iodide, 0.1% solution	10	20	—
CD3, Mydochrome	10	12	—
Droxychrome	—	—	5
Diethyl-p-phenylene-diamine sulphate	—	—	—
Water to	1000	1000	1000
pH	11.4-11.6	11.6-12.0	11.6-11.8

\*Substitute formulae from British Journal of Photography Annual (1977).

\*\*35% solution: 35 g. benzyl alcohol, 45 ml. diethylene glycol, made up to 100 ml. with water.

**Notes:** Extreme caution should be exercised in the preparation and use of the solutions. All contact with skin by the processing solutions and the individual ingredients should be avoided.

**LXVII.—BLEACH-BATHS FOR COLOUR REVERSAL PROCESSING\***

	277 <i>Kodak</i> E3	278 <i>Kodak</i> E4	279 <i>Agfa-</i> <i>chrome</i>
Potassium ferricyanide	80	112	80
Potassium ferrocyanide	—	—	—
Potassium bromide	20	24	20
Disodium phosphate, cryst.	25	45	20
Monosodium phosphate, anhyd.	—	12	—
Sodium acetate, cryst.	—	—	—
Boric acid	—	—	—
Potassium alum	—	—	—
Sodium or potassium bisulphate	—	—	12
Sodium thiocyanate	—	10	—
Sodium carbonate, anhyd.	3	—	—
Water to	1000	1000	1000
pH	—	6.6-7.0	5.0-5.4

\*Substitute formulae from British Journal of Photography Annual (1977).

All these bleach-baths are based on ferricyanide-bromide and vary only in buffering salts and hardeners. Care should be taken when interchanging solutions because some contain hardening agents and others do not and different types of films may require different bleach and fixer formulations to ensure that these processes go to completion.

Table LXIX summarises the processing steps and formulae recommended for various types of reversal films.

After the final wash a stabilizer-wetting agent solution (Formula 293) is generally used which contains formaldehyde as the stabilizing and hardening agent and a 10% solution of

**LXVIII.—FIXERS FOR COLOUR REVERSAL PROCESSING\***

	280 <i>Kodak</i> E3	281 <i>Kodak</i> E4	282 <i>Agfa-</i> <i>chrome</i>
Sodium thiosulphate, cryst.	160	—	200
Ammonium thiosulphate	—	120	—
Formalin	—	—	—
Potassium metabisulphite	10	20	—
Sodium sulphite, anhyd.	—	—	10
Boric acid	—	—	—
Monosodium phosphate, anhyd.	4.5	—	—
Water to	1000	1000	1000
pH	4.4-4.8	4.5-4.9	6.0-7.0

\*Substitute formulae from British Journal of Photography Annual (1977).

**LXIX —COLOUR REVERSAL PROCESSING PROCEDURES**  
*Processing Steps and Formulae*

	KODAK E3 Ektachrome (E3) Ektachrome Professional	KODAK E4 Ektachrome-X High Speed Ektachrome*	KODAK E-6 Ektachrome 64, 200 Ektachrome 50, 160	AGFA Agfachrome 50S, 50L
1. Pre-hardener	—	No. 269, 3 min., 29.5 ± 0.5°C.	—	—
2. Neutraliser	—	No. 270, 1 min., 28-31°C.	—	—
3. First Developer	No. 266, 10 min., 24 ± 0.25°C.	No. 267, 6 min., 29.5 ± 0.25°C.	6 min., 38.0 ± 0.3°C.	No. 268, 18-20 min. 20 ± 0.5°C.
4. Rinse	½-1 min., 20-26°C.	—	2 min., 33-39°C.	30 secs., 16-20°C.
5. Stop-Bath	No. 271, 3-10 min., 20-26°C.	No. 272, 2 min., 28-31°C.	—	No. 273, 4 min., 18-20°C.
6. Wash	3 min., 20-26°C.	4 min., 27-32°C.	—	10 min., 16-20°C.
7. Re-expose	—	—	Reversal bath 2 min., 33-39°C.	—
8. Colour Developer	No. 274, 15 min., 20-26°C.	No. 275, 9 min., 27-32°C.	6 min., 38.0 ± 0.6°C.	No. 276, 14 min., 20 ± 0.5°C.
9. Wash	5 min., 20-26°C.	—	—	20 min., 16-20°C.
10. Stop-Bath	Clear 2% Meta- bisulphite, 20-26°C.	No. 272, 3 min., 27-32°C.	Conditioner, 2 min., 33-39°C.	—
11. Wash	5 min., 20-26°C.	3 min., 27-32°C.	—	—
12. Bleach-Bath	No. 277, 8 min., 20-26°C.	No. 278, 5 min., 27-32°C.	6 min., 33-39°C.	No. 279, 5 min., 18-20°C.
13. Wash	1 min., 20-26°C.	—	—	5 min., 16-20°C.
14. Fixer	No. 280, 4 min., 20-26°C.	No. 281, 6 min., 27-32°C.	4 min., 33-39°C.	No. 282, 5 min., 18-20°C.
15. Final Wash	8 min., 20-26°C.	6 min., 27-32°C.	4 min., 33-39°C.	10 min., 16-20°C.
16. Stabilizer-Wetting Agent	1 min., 20-26°C.	1 min., 27-32°C.	30 sec., ambient	1 min., 18-20°C.
17. Drying	For safety air temperature should not exceed 36°C.			

\*Also suitable for: *Cilchrome, Fujichrome R-100, Sakuracolor R-100, 3M Color Slide 100 ASA.*

any of the following wetting agents to speed drying and to avoid drying marks:

Aerosol OT (Cyanamid)  
Tergitol 7 (Union Carbide)  
Tergitol NPX (Union Carbide)  
Invitol (Ciba)

**283.—STABILIZER BATH (E. GEHRET)**

Wetting agent, 10% solution	5-10 ml.
Formalin	5-10 ml.
Water to	1000 ml.

**GENERAL SUMMARY OF OPERATIONS FOR COLOUR  
PROCESSING AND CAPACITY AND LIFE OF SOLUTIONS**

In colour processing the essential steps are those connected with the actual production of the picture, i.e. the colour development itself and also the black-and-white (first) development for reversal materials. As indicated before, there are no universal formulae for these steps, and it is imperative to use the formulae recommended for the make of film in question.

The subsequent operations—stop-bath and/or wash—are also a sequence specific to individual makes and should not be altered, either. They are especially critical in processing negative colour films where the step after development is either a stop-bath or an extended wash, and one cannot replace the other. The purpose of a wash of 15 minutes or so is not only to remove developer and by-products from the film, but at the same time to allow a considerable degree of after-development to take place. This is essential to achieve the colour balance of the negative. On the other hand, in cases where a stop-bath is stipulated, one would again seriously interfere with the colour balance of the negative by omitting it and just carrying on with a wash.

As was mentioned earlier the steps after that are critical for some types of colour negative film (especially Agfa) as the mask is formed in the bleach-bath. Otherwise, the main function of the processing steps following colour development is to remove the “unwanted” products—silver and unchanged silver halide.

Here then is a summarised sequence of operations for colour negative films and the approximate times for each step:

- (1) Colour development (see Table LX) as recommended for the individual material.

- (2a) Rinse, stop-bath or stop-fix bath (see Formula 255) for 5 minutes and a 5-minute wash; or
- (2b) Extended wash as recommended for the film used.
- (3) Bleach or bleach-hardener (Table LXI) for 5-10 minutes.
- (4) Wash for 5 minutes.
- (5) Fix in 20% hypo cryst. (see Table LXII) for 5-10 minutes.
- (6) Final wash for 10 minutes.

Steps 2a-5 may be replaced by a combined bleach-fix solution (see page 374).

This is the sequence for colour reversal films:

- (1) First development (see Table LXIV) as recommended for the individual film.
- (2a) Rinse, stop-bath and hardener (see Table LXV) for 5 minutes, wash of 5 minutes, or
- (2b) Extended wash.
- (3) Re-exposure.
- (4) Colour re-development (see Table LXVI) as recommended for the film used.
- (5) Rinse, stop-bath (see Table LXV), and wash for 5 minutes.
- (6) Bleach or bleach-hardener (Table LXVII) for 8-10 minutes.
- (7) Wash for 5 minutes.
- (8) Fix in 20% hypo cryst. (see Table LXVIII) for 5 minutes.
- (9) Final wash for 15 minutes.
- (10) Stabilizer for 1 minute.

In reversal processing the steps following the colour development are less critical than in the processing of negative colour films.

The shelf-life of the colour developer solutions is about two weeks but if they are made up without the developing agent they may keep for two months or more. The majority of the other solutions will keep for about six months.

As an approximate guide one litre of developer will develop five 135-36 films, while bleaches and fixing solutions can process at least ten.

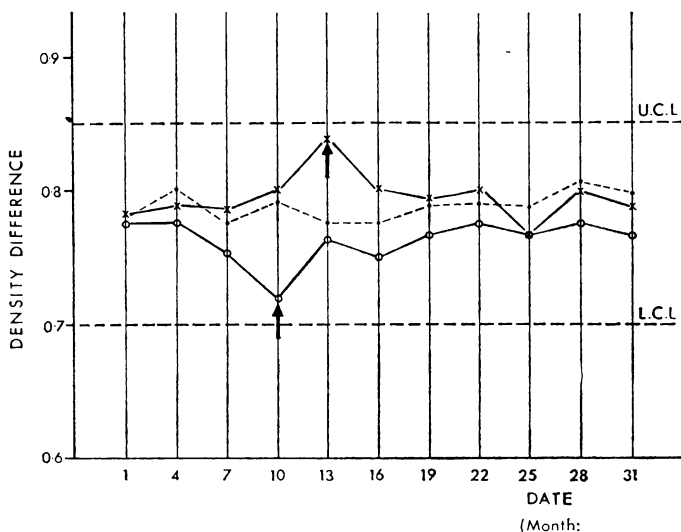
## *Quality and Environmental Control*

For the photofinisher it is of primary importance that negatives are uniformly and correctly processed. Unless film development is controlled within carefully defined limits, consistent print quality is not possible. Moreover, uniform negative development is important to operating costs; it reduces the number of reprints and economises on the usage of chemicals. Correct development also helps to retain the usefulness of many underexposed or overexposed negatives, resulting in a greater number of acceptable prints.

Control of development involves time, temperature, agitation and development activity. All of these effect, as we know from previous chapters, the overall density and contrast of the images. Although the average degree of replenishment recommended for tank development (see page 76) keeps the activity of the solution reasonably constant, variable factors such as considerably different carry-over rates from plant to plant make it necessary to test the activity of the developer at regular intervals throughout its life. For this purpose, test strips are supplied. These are pre-exposed strips of film with either two control spots or a number of density steps. They are developed at regular intervals together with negatives and then measured with a densitometer. The result gives a numerical measure of the activity of the developer from which the necessary degree of replenishing can be deduced.

Another important feature of large-scale processing of photographic materials is the control of pollution. The large-scale processing laboratory has to comply with legislation, either local or national, concerning the nature and amounts of chemicals that can be discharged into the urban sewage system, river, lake or sea. Fortunately the photographic industry is relatively clean and produces only a small amount of pollution when compared with other industries. However it is essential that the large-scale user of photographic chemicals is aware of the environmental effects of the chemicals that have to be discharged and how these effects can be minimised.

## PROCESS CONTROL CHART



The broken horizontal lines U.C.L. and L.C.L. represent the upper control limit of 0.85 and the lower control limit of 0.70.

The centre broken line shows the acceptable scatter of a process under control and no action is necessary.

The top full line shows that development activity is increasing and on the 13th of the month remedial action must be taken. The replenisher was therefore diluted and thereafter the process shows an acceptable random scatter. Conversely the bottom full line illustrates a decreasing developer activity which on the 10th day the replenisher was made more concentrated and thereafter the process is once more showing the normal scatter.

It is generally recommended that the developer activity is adjusted by varying the replenisher dilution rather than by adjustment of time or temperature of development as trends are cumulative.

## PROCESS CONTROL CHART

The test strips should be processed in the middle of a batch of films, if possible in the same position in the tank each time, as this represents the average development conditions for the films. After processing of the strip the densities of the low density spot and the high density spot are measured with a densitometer. Subtraction of the low density value from the

high density value gives a figure which must be within the range defined by the manufacturer (0.70-0.85 for the Kodak DN-13 system). This gives an approximate measure of the contrast. The figures obtained from control strips processed at various intervals of time (such as twice a week) are plotted against time to give a *process control chart*. It is of the utmost importance to take remedial action as soon as a discernible upward or downward *trend* is shown in the process control chart. If the process exceeds the control limits (set by the manufacturers) it is too late to take action and the process has got out of control with the result that many negatives are ruined. The accompanying process control chart shows when and where action should be taken (page 387).

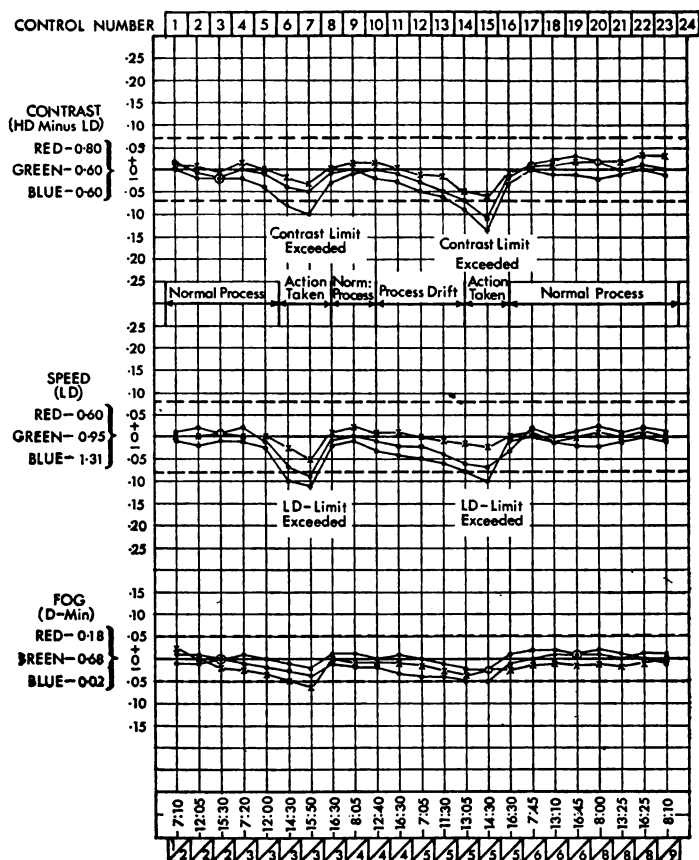
#### COLOUR PROCESS CONTROL

The control of colour negative processing is much more complicated since there are at least six stages (see page 375) as opposed to three for black and white processing. Also a colour negative has three colour images containing magenta, cyan and yellow dyestuffs requiring measurements of densities through green, red and blue filters of the densitometer. For quality control of a colour negative process (e.g. Kodak C-41) three density patches are generally used each read through the three filters of the densitometer (nine readings). These three density patches correspond to a high density (HD) a low density (LD) and a minimum density (D-min.). HD minus LD gives an approximate measure of the contrast, LD gives an approximate measure of the speed and D-min. gives an approximate measure of the fog for each of the three layers. In practice these readings obtained from the control strip, developed with the films, are subtracted from HD minus LD, LD and D-min. values obtained from a control strip processed by the manufacturer and supplied with the un-processed control strips. This gives either positive or negative values which are then plotted against the date on the process control chart.

The action required to be taken by the process controller when the control is about to be (or is) exceeded is very complex because of the number of solutions and variables. The reader is therefore recommended to consult the manufacturer's booklet on process control for the particular film types being processed (e.g. Kodak C-41, E-4, E-6, Agfachrome P-41 etc.).



# COLOUR PROCESS CONTROL CHART



The above diagram represents a typical colour process control chart (Kodak C-41 process).

## POLLUTION BY PHOTOGRAPHIC CHEMICALS

Almost any chemical may be toxic to living organisms when present in sufficiently high concentration for a long enough time under certain conditions. Toxicity is a relative term and water treatment authorities specify permissible concentrations of certain chemicals so that the micro-organisms and bacteria that are an essential part of the water purification process are not destroyed. Also it is essential that chemicals discharged into rivers, either directly or after going through the water treatment process do not kill fish, encourage the rapid growth of algae and that any recovered sewage sludge used for agricultural purposes is harmless.

Many chemicals used in the processing of photographic materials may not in themselves be toxic but are toxic to fish and micro-organisms because on breaking down they consume dissolved oxygen from the water (i.e. are *biodegradable*). The presence of oxygen is essential for the life of fish and micro-organisms. Two methods are (commonly) used to define this effect. These are: *Biochemical Oxygen Demand (BOD)* and *Chemical Oxygen Demand (COD)*.

Biochemical Oxygen Demand is normally expressed as the difference in the amount of dissolved oxygen measured immediately and after five days for a sample of effluent that has been seeded with the stream water into which the waste will eventually be discharged. These are referred to as (BODs) values and normally expressed in grams or milligrams of dissolved oxygen consumed per litre of effluent.

Chemical Oxygen Demand is a quantitative measure of the amount of oxygen needed to oxidise a chemical under controlled laboratory conditions using potassium dichromate as the oxidising agent (Analysis of Raw, Potable and Waste Waters, Her Majesty's Stationery Office, London 1972). COD is expressed in grams or milligrams of oxygen absorbed per litre of effluent from the standard dichromate solution. The measurement of COD values is more reproducible than BOD values and generally has a higher value than BOD<sub>5</sub>.

Photographic processing laboratories normally are not required to undertake such analyses but may be required to estimate BOD<sub>5</sub> or COD values for their wastes from published values provided by the manufacturers of photographic chemicals (see Tables LXXI and LXXIII).

Photographic chemicals vary in their rates of biodegradability and may be classified broadly into the following three categories:

- (1) rapidly biodegradable, e.g. acetate, benzyl alcohol, hydroquinone, sulphite and thiosulphate,
- (2) slowly biodegradable, e.g. ammonium salts, citric acid, formaldehyde, formic acid, glycols, hydroxylamine and developing agents,
- (3) non-biodegradable, e.g. borate, bromide, dichromate, ferricyanide, ferrocyanide, nitrate, and phosphate.

However some of the above chemicals are harmful for reasons other than their biodegradability. Ideally processing chemicals should be non-biodegradable and have no other harmful effects. But in reality processing necessitates the use of chemicals that are biodegradable and harmful to the environment. The undesirable effects of some typical photographic ions and compounds are given below:

#### *Ammonium salts*

Modern rapid fixers produce relatively high concentrations of ammonium ions in effluents. If the effluent has a pH value greater than about 8 ammonia will be produced and some authorities limit the ammonia content to 2 mg./l. if the pH is greater than 8. Ammonium ions are biodegradable but if they appear in streams may be converted to nitrate which is a nutrient (see below).

#### *Borates*

Borate ions are particularly toxic to certain plants. Fortunately their dilution by the wash water usually reduces their concentration to an acceptable level and calcium present in hard water may precipitate them.

#### *Dichromates*

Chromium ions in waste from dichromate bleaches are toxic to aquatic life. However it is precipitated as chromium hydroxide when mixed with alkaline processing effluents that contain sulphite, and at normal dilution should not cause any difficulties to the water purification process. Some authorities limit the amount of chromium present in the effluent and it is

then necessary for the dichromate bleach to be collected and disposed of separately.

### *Ferricyanides and ferrocyanides*

Some bleaches for colour processes use ferricyanide rehalogenizing bleaches. In dilute solution, under the influence of air and sunlight, they are converted to cyanide which is extremely toxic although it is present only in very small amounts. Therefore these bleaches should be regenerated and re-used to minimise the amounts discarded (see page 396). The ferricyanide bleach is, for many colour processes, being replaced by formulae based on iron sequestrene that are substantially less harmful and capable of easy regeneration and re-use.

### *Hydroquinone*

Hydroquinone is toxic to fish at a concentration as low as 1 mg./l. Fortunately hydroquinone is rapidly degraded in the water treatment plant.

### *pH values*

The pH value of the effluent from a processing laboratory is generally between 7 and 9 which is well within the limits set by the water-treatment authorities. This is achieved by the normal mixing of acidic and alkaline wastes from photographic processing machines.

### *Phosphates and nitrates*

Phosphates and nitrates are non-biodegradable, and act as nutrients, encouraging the growth of algae and weeds in streams. A few processing solutions contain trisodium phosphate buffers, and many contain metaphosphate to reduce sludging by hard water. The amounts of phosphates and nitrates present are usually small and should not cause environmental problems.

### *Silver and other toxic metal ions*

Free silver ions are toxic to micro-organisms at a very low concentration and as we saw earlier (page 282) are removed also for economic reasons. The small amount of silver present in the final wash water is in the form of the less harmful argentothiosulphate that breaks down to form insoluble silver sulphide in the water-treatment plant.

Other toxic metals such as barium, copper, cadmium, lead, mercury, and nickel are not present in any significant amount in processing effluents.

Water-treatment authorities specify acceptable limits for certain chemicals and these may include phenols, silver, heavy metals, borates, phosphates and cyanides. Also limits for pH value, colour, odour, suspended solids, oils, tars, and detergents may be specified.

Table LXX gives the characteristics of a typical processing waste. It can be seen that the most significant contribution to pollution is the oxygen demand, the remainder of the characteristics normally fall well within the specified limits.

**LXX.—CHARACTERISTICS OF A TYPICAL PROCESSING WASTE**

<i>Characteristic</i>	<i>Amount</i>
Temperature	32°C., or less
Oils, greases or tars	none
Suspended solids	less than 0.03 g./l.
Colour	slight
Odour	negligible
Flammability	zero
Detergents	minimal
pH value	7-9
phenols	none (excluding hydroquinone)
BOD <sub>5</sub>	0.15-0.60 g. O <sub>2</sub> /l.
COD	0.18-1.0 g. O <sub>2</sub> /l.

#### CALCULATION OF BOD<sub>5</sub> (OR COD)

Table LXXI lists BOD<sub>5</sub> values for the more commonly used photographic chemicals. From such tables it is possible to estimate the total BOD<sub>5</sub> values for processing solutions whose formulations are known.

However it should be borne in mind that estimates of BOD<sub>5</sub> using the data of Table LXXI for individual chemicals or that of Table LXXIII for prepacked chemicals are estimates and apply only to *fresh* solutions. It is impossible to predict with certainty the BOD<sub>5</sub> values for used solutions and the values that occur when different processing solutions are mixed before discharge. Although it is possible to take into account the dilution of effluents. Such estimates serve as a useful guide to the processing laboratory for determining whether specified limits may be exceeded.

**LXXI.—BOD<sub>5</sub> VALUES FOR PHOTOGRAPHIC CHEMICALS\***

<i>Chemical</i>	<i>grams BOD<sub>5</sub> per gram of chemical</i>
Acetic acid, glacial	0.74
Ammonium thiocyanate	< 0.010
Ammonium thiosulphate, 58% solution	0.36
Benzyl alcohol	1.80
Borax, decahydrate	0
Boric acid, anhyd.	0
Citrazinic acid	< 0.010
Citric acid, monohydrate	0.39
Colour developing agent, Kodak CD-1	0.13
Kodak CD-2	0.15
Kodak CD-3	0.10
Kodak CD-4	0.13
Disodium phosphate	0
Ethylenediamine	0.02
Ethylenediaminetetra-acetic acid, disodium, dihydrate	0.025
Ethylene glycol	0.41
Formalin	0.37
Hydroquinone	1.12
Metol	0.75
Monosodium phosphate, anhyd.	0
Phenidone	0.16
Potassium alum, decahydrate	0
Potassium dichromate, anhyd.	0
Potassium ferricyanide, anhyd.	0
Potassium persulphate	0
Sodium acetate, anhyd.	0.59
Sodium bisulphate	0
Sodium bromide	0
Sodium carbonate, anhyd.	0
Sodium chloride	0
Sodium citrate, dihydrate	0.35
Sodium dihydrogen phosphate, monohydrate	0
Sodium ferrocyanide, decahydrate	0
Sodium hydroxide	0
Sodium metabisulphite, anhyd.	0.154
Sodium sulphate	0
Sodium sulphite	0.12
Sodium thiocyanate	0.02
Sodium thiosulphate, pentahydrate	0.20
Sulphuric acid	0
Trisodium phosphate, 12 H <sub>2</sub> O	0

\*Data from Eastman Kodak Publication J-41.

The actual measurement of BOD<sub>5</sub> (or COD) is best carried out by the water-treatment authority on samples of waste leaving the laboratory.

Provided that the formulation of the processing solutions are known it is possible to estimate the total BOD<sub>5</sub> value for the effluent from the processing machine (or machines) using the data given in Table LXXI. Let us consider as an example a black-and-white negative process using D76 developer (Formula 80, page 206) a stop bath (Formula 178, page 271) and a fixer (Formula 162, page 264). Firstly the BOD<sub>5</sub> values for the individual chemicals are added together as shown in Table LXXII.

**LXXII.—ESTIMATION OF BOD<sub>5</sub> FOR PROCESSING SOLUTIONS PREPARED FROM INDIVIDUAL CHEMICALS**

<i>Chemical</i>	<i>Concentration (g./l.)</i>	<i>BOD<sub>5</sub> (g./g. of chemical)</i>	<i>BOD<sub>5</sub> (g.)</i>
<i>Developer:</i>			
Metol	2	0.75	1.5
Sodium sulphite, anhyd.	100	0.12	12.0
Hydroquinone	5	1.12	5.6
Borax	2	0	0
<i>BOD<sub>5</sub> for developer</i>			<u>19.1 g./l.</u>
<i>Stop bath:</i>			
Acetic acid, glacial	17	0.74	12.58
<i>BOD<sub>5</sub> for stop bath</i>			<u>12.58 g./l.</u>
<i>Fixer:</i>			
Sodium thiosulphate, cryst.	240	0.20	48.0
Sodium sulphite, anhyd.	10	0.12	1.2
Sodium metabisulphite	25	0.154	3.85
<i>BOD<sub>5</sub> for fixer</i>			<u>53.05 g./l.</u>

Therefore a simple calculation enables us to find the contribution to the BOD<sub>5</sub> value of the effluent. The first column is the known concentration of the chemical, the second column is BOD<sub>5</sub> value for the chemical, and multiplying one figure by the other gives the contribution by that chemical in the third column. Summing the values of the third column gives the contribution to BOD<sub>5</sub> by the particular solution.

If, for example, a processing laboratory is required to estimate the BOD<sub>5</sub> of their waste over one week then it is necessary to know the volumes of the individual solutions and wash water used over this period. Using the example of the process given in Table LXXII and say, 5 litres of developer, 1 litre of stop bath and 2 litres of fixer are used over this period, together with 1200 litres of water, the total BOD<sub>5</sub> for the effluent is given by:

$$\frac{(5 \times 19.1) + (1 \times 12.58) + (2 \times 53.05)}{5 + 1 + 2 + 1200} \text{ g. O}_2/\text{l.}$$

$$= 0.18 \text{ g. O}_2/\text{l.}$$

COD values may be estimated in an exactly similar way.

#### LXXIII.—BOD<sub>5</sub> VALUES FOR PREPACKED PROCESSING SOLUTIONS

<i>Processing solution</i>	<i>BOD<sub>5</sub> (g./l.)*</i>
<i>Du Pont</i>	
6D fine-grain film developer	17
16D film developer	10
21D litho developer	29
53D all purpose developer	6
XIAD Cronex industrial automatic developer	74
18F universal fixer	59
XIAF Cronex industrial automatic fixer	70
<i>Ilford</i>	
Autophen developer (concentrate)	34
ID-11 fine-grain developer (stock)	19
Ilfolith DL lith developer	38.5
Microphen fine-grain developer (stock)	18
Perceptol ultra fine-grain developer (stock)	16
PQ Universal developer (concentrate)	51
IF-23 fixer (concentrate)	128
Ilfofix (stock)	80.6
Hypam rapid fixer (1 + 4)	57.6
<i>Kodak</i>	
D-8 high contrast developer	61.1
D-11 high contrast developer	20.4
D-19 high contrast developer	21.6
D-76 fine-grain developer	19.6
Kodalith Super lith developer	41.9
Versamat developer replenisher type B	20.4
Versamat developer starter type B	110
X-Omat developer replenisher (medical)	50.3
F-5 fixer	60
Rapid fixer	37.1
Versamat fixer and replenisher type B	37.1
X-Omat fixer and replenisher (medical)	63.5

\*The BOD<sub>5</sub> values given refer to working strength solution unless indicated otherwise and have been obtained from manufacturer's data.



More usually BOD<sub>5</sub> (or COD) values are calculated from manufacturers data for pre-packed chemicals that are normally used in large scale processing. In this case similar calculations are carried out using the known values for BOD<sub>5</sub> or COD for the chemical packs. Table LXXIII gives BOD<sub>5</sub> values for some representative examples of pre-packed chemicals. Thus in general BOD<sub>5</sub> for the waste is obtained by:

$$\text{BOD}_5 (\text{total}) = \frac{\text{total BOD}_5 \text{ for solutions}}{\text{volume of solutions discarded} + \text{volume of water used}}$$

This method of using the BOD<sub>5</sub> values of the pre-packed chemicals is obviously quicker than working with values for the individual chemicals. It also is less likely to lead to calculation errors.

#### METHODS OF MINIMISING POLLUTION

It could be argued that diluting the chemicals discarded from photographic processes with water will reduce the harmful effects. Whilst this is true, water is a scarce and expensive commodity that must be conserved whenever possible, and diluting the wastes also increases the total load placed by the laboratory on the water-treatment laboratory plant. For those reasons dilution is not a recommended method for minimising pollution.

However some dilution does take place in the normal operation of a photographic processing machine. The volume of wash water used is at least 50 times greater than the volumes of developer and fixer discarded when batch replenishment is used, and at least 350 times greater when continuous replenishment is used.

Perhaps the most important contribution to minimising pollution is to operate photographic processing equipment as efficiently and carefully as possible. Such methods involve the following considerations:

- (1) *Good laboratory practice.* This means keeping stock solutions and replenishers in sealed containers. Also, whenever possible, using floating lids on tanks to minimise aerial oxidation and so extending the useful life of developers.

- (2) *Quality control.* This involves the use of minimum replenishment to maintain the solution activity, and the use of quality control charts to take the appropriate action to keep the process in control.
- (3) *Reduce solution carry-over.* The use of efficient squeegees in processing machines between the various solutions reduces solution carry-over. This enables lower replenishment rates to be used thus reducing the amount of waste.
- (4) *Regeneration of solutions.* Whenever possible solutions should be regenerated and re-used. This has long been the practice for fixers from which the silver is recovered, and the solution re-used after appropriate additions have been made. A bleach used in colour processes may be regenerated by oxidising the ferrocyanide back to the original ferricyanide form with ammonium or potassium persulphate. The modern bleaches based on iron sequestrane are inherently less harmful than those based on ferricyanide and may be regenerated by aerial oxidation. Also bleach-fixes using iron sequestrane may be recovered in a similar manner. Silver is recovered from fixes and bleach-fixes by using the steel wool method (page 288) or the electrolytic method (page 285).
- (5) *Use of balancing tanks.* To ensure that the maximum dilution of waste chemicals is achieved a balancing tank may be installed in the waste line. This should have a capacity of several hours water usage and should be constructed such that there is a good mixing of the chemicals discarded with the wash water. Such tanks act as a "buffer" preventing large changes of concentration of the effluent.
- (6) *Use of holding tanks.* On occasions it may be necessary to dump large volumes of processing solutions due to an emergency or shut-down of a machine for overhaul. If large volumes of solutions were to be discarded the permissible amounts of the chemicals in the effluent would be exceeded. To avoid this happening, a holding tank must be used sufficiently large to take the waste chemicals. From

the tank they can then be slowly bled to the drains at a rate roughly equal to the normal overflow rate for that solution.

#### WATER CONSERVATION

A number of methods are available for ensuring that the minimum amount of water is used in processing whilst not reducing washing efficiency. Water that is used for cooling or heating should not be run off as waste but should be re-used. This can be achieved by using a closed-circuit system with the appropriate heating or cooling units, or by using the water for processing after it has been filtered. The water flow should be controlled by regulating valves that automatically "shut off" when a wash tank is not in use. Also efficient squeegees before washes will reduce the amount of chemicals carried over from the preceding tank, and therefore reduce the amount of water needed for efficient washing.

Savings in water can be achieved using countercurrent washing tanks in which water enters the last of a series of wash tanks and then goes into the next tank in the opposite direction to the film travel. As the film goes through the wash tanks it encounters cleaner and cleaner water.

Installing a salt bath before the final wash can considerably reduce the amount of wash water required. Eastman Kodak recommend a solution containing a mixture of sodium sulphite and sodium metabisulphite as a total combined concentration of 20 g./l. and a pH of 8-9.

The recommended washing times for most processes have a safety factor and it may be possible to shorten these times without leaving chemicals in the film. However, any materials processed using shorter washing times should be checked for residual chemicals using the hypo and silver test solutions given on pages 291 and 292, or those given in the Eastman Kodak publication S-39.

## *Preserving the Negative*

Negatives are valuable. They are originals and frequently irreplaceable. As they also tend to be fragile and easily marked, they must be stored in a manner that protects them from physical, chemical and atmospheric damage.

### PLATE AND FLAT-FILM NEGATIVES

These are best stored in transparent envelopes of parchment or Cellophane, upon which a consecutive number is marked or sufficient detail to identify the negative by. The envelopes with their negatives can be kept in plate or film boxes which bear on their cover details of the contents, or the boxes may be stacked in book-form on shelves and have labels on their ends. The orderly and precise worker will have a catalogue of his negatives which will contain their consecutive number and description.

A much more costly method is to keep the negatives in racked wooden boxes, but this usually involves more room, as well as expense, than the average photographer desires to afford.

### ROLL-FILM NEGATIVES

In roll form, films are almost certain to suffer damage and they may also collect dust and grit. They should therefore always be preserved flat—cut either into single negatives or, in the case of 35 mm. films, into five or six negatives at most.

Here again parchment or Cellophane envelopes should be used, marked with the negative number or detail and preserved in larger envelopes or in boxes.

All negatives should be kept in suitable conditions. That is in a dry, cool place not subject to any wide variations of

temperature and well clear of any fumes from fireplaces, gas fires or the like.

## CLEANING FILM

Dirty and dusty or greasy film can be cleaned:

### 284.—FILM CLEANER

Acetic acid	1 part
Vaseline	5 parts
Carbon tetrachloride	100 parts

The solution is applied either with chamois leather or viscose sponge. Shake the solution well before using it. The film is lightly rubbed with the solution, being careful not to exert any serious pressure. After about 10 minutes the film is then dried with a soft clean chamois leather until every perceptible trace of the cleaner is removed, and the film appears quite dry.

## DEALING WITH SCRATCHES AND ABRASIONS ON FILM

The trouble can be overcome comparatively simply so that the scratches are rendered imperceptible. The method consists in coating the film with a thin solution of gelatine which fills in the scratches and renders them incapable of affecting the optical properties of the film during printing.

### 285.—ANTI-SCRATCH SOLUTION

Water	20 ounces	500 ml.
Chloral hydrate*	2 ounces	50 grams
Gelatin	$\frac{1}{2}$ ounce	12.5 grams

\*Caution, irritant to skin and eyes.

The chloral hydrate is dissolved first, then the gelatin, in small pieces, is allowed to swell in the cold and when swollen the whole is warmed on a water bath and stirred until solution is complete.

The temperature should not exceed 140°F. (60°C.).

The solution, which has reasonably good keeping properties, should be used at about room temperature.

# Dark-Room Hints

## ANTIDOTES FOR POISONS

*Against Acids:* Alkaline drinks, i.e., sodium bicarbonate, magnesium carbonate or a suspension of magnesium oxide. If these are not available, then quantities of warm water to induce vomiting. Milk and oil may also be used.

*Acid splashes in the eyes:* Wash with warm water or with very dilute sodium bicarbonate solution.

*Against Caustic Alkalies:* Drink strongly diluted vinegar of citric acid or apple juice. Suck pieces of ice. Milk or oil may be drunk.

*Alkali splashes in the eyes:* Wash with water or very dilute boric acid.

*Gas Poisoning:* Fresh air, remove constricting clothing, artificial respiration.

*Mercury Poisoning:* Milk and white of egg.

## PREVENTION OF DERMATITIS

As a preventive against dermatitis caused by metol to especially sensitive persons, the fingers may be rinsed both before and during development in:

### 286.—PREVENTIVE AGAINST METOL DERMATITIS

Hydrochloric acid  
Water

1 part  
500 parts

It is always better to avoid dermatitis either by wearing protective gloves or by using solutions that do not contain the particular chemical to which one is allergic.

## REMOVING DEVELOPER STAIN FROM THE HANDS

Rub the hands well with a

### 287.—STAIN REMOVER

1% solution of potassium permanganate

until they have taken on an overall brown colour, then wash well in the ordinary way and finally rinse in a

**288.—CLEANSER**

Strong solution of sodium bisulphite

which will completely remove the brown colour.

**REMOVING DEVELOPER SPLASHES FROM CLOTHES**

Damp the spots or splashes with

**289.—STAIN REMOVER**

5% solution of potassium permanganate

Allow to remain for a few moments and then decolorise with

**290.—CLEANSER**

10% solution sodium bisulphite

In the case of coloured cloth or fabric, care must be exercised, otherwise the treatment may cause the appearance of a bleached area.

**CLEANING SOLUTION FOR ALL NON-METAL VESSELS**

**291.—VESSEL CLEANSER**

Water	40 ounces	1000 ml.
Potassium dichromate	4 ounces	100 grams
Sulphuric acid conc.	4 ounces	100 ml.

Dissolve the dichromate first and then add the acid slowly and with constant stirring as great heat will be evolved. When this solution has been used the vessels must be well washed with plenty of water.

**RELEASING JAMMED GLASS STOPPERS**

Quickly but carefully warm the neck of the bottle with a gas or spirit lamp flame. Then tap the stopper with a piece of wood until loosened. Where the jamming of the stopper is due to crystallising of salts out of solution a drop or two of water is a help, or the bottle may be inverted and placed in warm water up to the neck of the bottle.

## DISINFECTING OF WOOD AND COMPOSITION TANKS

Large tanks often develop a black deposit after some time in use, which harbours bacteria and causes evil smelling gas to be given off. Such tanks can be disinfected as follows.

### 292.—DISINFECTANT

Remove all metal parts such as hangers, rods and the like, then fill the tank with water, add a quart (1 litre) of commercial hydrochloric acid, stir in about 4 ounces (100 grams) chloride of lime.

Put the lid on the tank and leave it over night, preferably out of doors. Next day empty the tank and wash out well with plenty of water.

## SAVING CRACKED OR BROKEN PLATES

(1) *The Film is Undamaged:* It should be separated from the glass as follows. Harden the film for 15 minutes in

### 293.—HARDENING BATH

10% solution of formalin in water

Then with a sharp knife cut round the edge of the film about 1/16th-inch (2 mm.) inside the edge of the plate, wash the plate free from formalin solution and place in a dish with the following:

### 294.—PLATE STRIPPING SOLUTION

Water	4 ounces	100 ml.
Ammonium bifluoride	40 grains	2 grams
Sulphuric acid, 10% solution	5 drops	5 drops

After about two minutes the film can usually be stripped off the glass. It is washed carefully in water and floated on to another plate. If preferred, this can be a normal plate, fixed but undeveloped, in which case the gelatine film holds the stripped film firmly.

(2) *The Film is Damaged:* In this case the broken pieces must be cemented together:

### 295.—CEMENT

Water glass or Canada balsam thinned down with benzene

The broken pieces of glass have their edges painted with the cement and are then carefully fitted together on a glass plate and allowed to dry.



## GIVING GREATER TRANSPARENCY TO PAPER NEGATIVES

The back of the negatives should be well rubbed with a very thin clear machine oil of the kind used for typewriters or sewing machines. If necessary the oil can be thinned with a little clear paraffin oil. Care should be taken not to use any excess of oil beyond that required to render the negative transparent. Warming helps.

## WRITING ON NEGATIVES

(1) *To Reproduce Clear Writing on Dark Ground:* On a well-gelatined strip of paper write the necessary text with a

### 296.—WRITING SOLUTION

Concentrated solution of potassium ferricyanide

and allow it to dry. Then damp the negative surface by soaking, remove all superfluous moisture and lay the gelatined paper on the negative with the writing against the negative film; leave for one minute and then remove and wash.

(2) *To Reproduce Black Lettering on the Negative:* The necessary text is written in waterproof ink on thin Cellophane which is then cemented on to the negative with the written side in contact with the negative film.

# Defects in Negatives

## FAULTS IN THE GRADATION OF THE NEGATIVE

(1) *The negative lacks detail in the shadows and density in the highlights.*

The usual cause is under-exposure (page 34).

If there is perceptible detail in the shadows, then some improvement may be effected by intensification (page 347).

(2) *The negative is thin and flat, but there is reasonable detail in the shadows.*

The negative has been correctly exposed but has been under-developed.

(a) Development was too short (page 38).

(b) The developer was exhausted or too heavily diluted (page 140).

(c) The temperature of the developer was too low (page 72).

Intensification or the choice of a hard gradation paper, or both, should produce reasonably satisfactory pictures (page 347).

(3) *The gradation of the negatives is flat and the shadows fogged. The parts of the plate or film protected from light, particularly the edges, are however clear.*

The negative has been over-exposed. A somewhat similar fault develops in negatives of subjects taken against the light when parts of the subject have been too brilliantly lighted (page 34).

The best remedy is the choice of a hard printing paper (page 339). Where a shorter exposure, either for printing or enlarging is desired, the use of Farmer's reducer for clearing the shadows will also help by increasing the general contrast (page 342).

(4) *The negative is hard and has heavy, dense highlights.*

It has been over-developed.

- (a) Development was carried on for too long.
- (b) The developer was too strong or contained too much alkali.
- (c) The temperature of the developer was too high.

Choose a soft paper (page 339) or use a superproportional reducer, i.e., ammonium persulphate, or both (page 344).

(5) *The negative is hard as in (4) and the shadows are fogged.*

The negative has been over-exposed (page 34) and also over-developed (page 38).

A soft paper should be used, but the shadows should first be cleared with Farmer's reducer (page 342) and then the whole negative reduced with persulphate (page 344).

#### THE NEGATIVE IS FOGGED

(6) *The negative shows grey fog all over, including those parts protected from light by the rebate of camera or dark-slide.*

- (a) Development is too long or too warm developer or lack of bromide (page 91).
- (b) Unsafe dark-room light, or stray white light in darkroom (page 122).  
Test safelight to ensure that it is suitable for the negative material being used.
- (c) Faulty sensitive material due to staleness, inappropriate storage, etc.
- (d) Aerial fog due to too much exposure to air during development; this can occur particularly in drum-development and when dish-development is used.

Desensitisation helps to reduce this possibility (page 251).

Use of a hard printing paper (page 339) may help, also clearing the fog with Farmer's reducer (page 342) followed later by intensification (page 347).

(7) *The edge of the plate or film shows a black fog which tails off towards the inside of the plate or film.*

- (a) Manufacturing fault or stale material, more common in plates than film.
- (b) In roll-film can occur through a loosely-wound spool being exposed to daylight during charging or emptying the camera.

(8) *Dichroic fog, appears red or violet by transmitted light and bluish or green by reflected light.*

- (a) Spent developer or developer contaminated with hypo (page 271).
- (b) Unsuitable developer (i.e. containing silver solvent such as potassium thiocyanate).
- (c) Developer too warm (page 107) or development too protracted. With fine-grain developers too high a sulphite content can cause the trouble (page 203).
- (d) Exhausted fixing bath, or fixing bath too warm and spent (page 268).
- (e) Fixing bath contains too much carried over developer (page 271).
- (f) Insufficient rinse between development and fixing, or exhausted stop-bath (page 271).
- (g) Negative exposed to white light before fixing was complete.

(9) *The negative shows yellow fog when examined by transmitted light.*

Causes similar to those detailed under dichroic fog.

*Removal of yellow and dichroic fog.*

1st Method: Harden the emulsion film in the following:

#### 297.—HARDENING BATH

Formalin	$\frac{1}{2}$ ounce	12 ml.-
Sodium carbonate, anhyd.	$\frac{1}{4}$ ounce	6 grams
Water np to	40 ounces	1000 ml.

Then wash for a moment or two and treat for 5 minutes in a  $\frac{1}{2}$  % solution of potassium permanganate, wash, fix in 30 % plain hypo, clear in 10 % bisulphite and wash finally.

2nd Method: Bathe the negative in the following solution.

#### 298.—FOG REMOVER

Thiourea	28 grains	1.4 grams
Citric acid	28 grains	1.4 grams
Water to make	5 ounces	125 ml.

(10) *Yellow fog which merges into brown.*

Caused by oxidation products in the developer, usually due to too low sulphite content (page 81). It may also occur when a fixing bath is exhausted and contaminated with developer (page 268).

To remove the fog harden the negative in the formalin bath given above, wash, bleach in the permanganate bleach made up as follows. Make up a solution containing:

### 299.—FOG REMOVER

Sodium chloride (common salt)	$\frac{1}{4}$ ounce	7 grams
Sulphuric acid conc.	20 minims	1.5 ml.
Water	4 ounces	100 ml.

Add to this just before use 4 ounces (100 ml.) of  $\frac{1}{2}\%$  solution of permanganate. Bleach for 3-4 minutes: the film will become covered with brown manganese dioxide which, after a good rinse, is removed by sodium bisulphite solution. Now wash the negative well and place in full daylight until it assumes a reddish colour and then re-develop it, using the amidol developer recommended by Kodak.

### 300.—AMIDOL RE-DEVELOPER

Water at 125°F. (52°C.)	30 ounces	750 ml.
Sodium sulphite, anhyd.	1 ounce	25 grams
Amidol	$\frac{1}{4}$ ounce	6.5 grams
Cold water to make	40 ounces	1000 ml.

(11) *The negative shows a red, blue or greenish coloration.*

Usually caused by the anti-halo layer (page 61).

The colouring can easily be removed by a weak alkaline solution, e.g., a diluted developer or water containing a few drops of ammonia.

### WHITE DEPOSIT ON OR IN THE FILM OF THE NEGATIVE

(12) *Fine-grained white deposit.*

Chalky residue from very hard water (page 92).

To prevent, use Calgon or similar compound in developer. To remove deposit, bathe negative in 2% acetic acid, then wash well. If this treatment causes a coloration of the negative, add a few drops of ammonia to the wash water.

(13) *Whitish deposit on the dried negative, which has a shiny appearance when wet.*

The deposit consists of aluminium sulphite derived from a hardening and fixing bath into which too much developer has been carried over.

The use of an acid stop bath helps here and lengthens the life of the hardening fixing bath (page 271). To remove the deposit, harden the film in alkaline formalin solution (page 377), and then treat the film in a 5 % solution of sodium carbonate, then wash well.

*(14) Pale yellowish-white appearance of negative. Opalescence.*

Due to decomposition of fixing bath and setting free of sulphur. The fixing bath contains too much acid, too little sulphite or is too warm (page 272).

To remove the opalescence harden the film in alkaline formalin solution (page 406), wash well and treat with a 10 % solution of sodium sulphite at a temperature of about 100°F. (38°C.).

#### DARK OR LIGHT STREAKS OR BLOTCHES ON THE NEGATIVE

*(15) Light or dark parallel streaks appearing, light streaks on dark parts and dark streaks on light parts of negative.*

Due to insufficient movement of developer during development, allowing local concentration of used-up developer (page 78).

*(16) Dark or light streaks originating where the plate or film holder touched the negative material.*

Dirty plate or film holder.

See page 401 for cleaning.

*(17) Scum markings.*

Dirty developer due to dust, etc.

*(18) Large irregular light areas with sharp edges.*

Unequal initial flow of developer over negative so that development was uneven.

*(19) Regular wave-like markings on negatives dish developed.*

Insufficient rocking of dish during development.

*(20) Sharply-defined areas of varying density.*

Too small an amount of developer in dish, also see (18).

*(21) Irregular areas of higher density.*

Variations in concentration of developer can be caused by adding concentrated or warm developer to tank or dish during development. This should never be done.

*(22) Irregularly-defined light areas, often contaminated with scum.*

Due to developer standing in tank unprotected from dust

and air. The surface becomes covered with a scum of oxidation products which gets on to the surface of the negative and locally hinders development.

If such scum is seen on the surface of the developer, the developer should be filtered or discarded.

#### SPOTS, FLECKS AND LINEAR MARKINGS

(23) *Thin black or light straight lines.*

Scratches due to abrasion. Often caused on roll film by dust or grit getting into the camera, or by careless loading of spools causing the film to jam when being wound through the camera. If the scratches are made before exposure they usually appear light; if after exposure they are darker than their surroundings.

(24) *Black irregular forked or branched wavy lines.*

Static markings caused by an electric charge being developed on the film. Usually caused in manufacture, but can occur in very cold and dry areas, if the film is carelessly handled and roughly wound up.

(25) *Strong black lines usually radiating from a corner or side of negative.*

Light leaks either in the front or the bellows of the camera.

(26) *Small, light, undefined brownish flecks.*

Over-used and insufficiently agitated tank developer.

(27) *Marbling-like or honeycomb markings on the film.*

Exhausted, insufficiently mixed or unstirred developer.

(28) *Clear, well-defined light round spots, sometimes with comet-like tail.*

Air bells on the film during the early stages of development.

(29) *Honeycomb markings with dark surrounds.*

Scum on the developer which has collected on the face of the negative.

(30) *Wrinkled film or reticulation.*

Too great a variation in temperature between baths, possibly too high a developer temperature followed by a cold fixing bath.

(31) *Small light or dark spots usually well defined.*

Ordinary or chemical dust which has settled on the negative before development.

(32) *Small dark or light flecks of irregular form.*

Particles of undissolved chemicals in the developer.

(33) *Holes in the film or hollows.*

A fault caused by bacteria or moulds, most common in summer when plates or films have been too long drying in a warm, moist atmosphere.

(34) *Light or dark drop-like markings on the film.*

(a) Spots of water which have fallen on a partially dry negative.

(b) Drops of water left on a negative when put to dry.

#### LESS COMMON NEGATIVE FAULTS

(35) *Small blisters covering the negative.*

Usually caused by carbon dioxide gas set free when the negative is transferred from the developer to a too-acid stop bath or an acid fixing bath.

(36) *Wrinkled emulsion at edges of film floating off support.*

Too high temperature developer or wide differences in the temperature of the different baths.

(37) *The numbers and other indications from the red or green-black paper of the roll-film appear as developed image on the film.*

Badly stored or stale film.

(38) *Partial or complete reversal of the negative into a positive image.*

Use of unsafe dark-room lighting (page 122) or accidental fogging with white light before exposure.

(39) *Partial melting of film during drying.*

Too high a drying temperature (page 294) and not sufficient air current.



# Photographic Chemicals

In the following pages, details are given of the more important photographic chemicals, arranged as follows.

- (1) The common name of the chemical, other names in use, chemical formula and British and American standards (BS and ANSI respectively).
- (2) Appearance, method of preserving, special properties, i.e., poisonous, corrosive or inflammable. Solubility in water at normal temperature (in case of developing agents in parts per 100=WS.). In the case of developing agents there is also given (a) Solubility in 100 parts 10% sodium sulphite solution S.S.S. and (b) Solubility in 100 parts of a mixture of equal volumes of sodium sulphite  $\frac{1}{2}\%$  and sodium carbonate  $\frac{1}{2}\%$  solutions, S.S.C., all at normal temperature, i.e., 65°F. (18°C.).
- (3) Use for photographic purposes, usually with page references.

ACETIC ACID GLACIAL.  $\text{CH}_3\text{COOH}$ . BS 576: 1950; ANSI PH 4. 100 (1958).

Water clear fluid with stinging smell. Solidifies at temperatures below 62°F. 17°C. Corrosive action.

Mixes in all proportions with water.

Used for stop bath (pps. 270-71), addition to fixing baths (page 274) and in uranium intensifier (page 350).

ALUM, POTASH. Aluminium potassium sulphate. Rock alum.

$\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ . BS 3312: 1961; ANSI PH 4. 150 (1958).

Colourless transparent crystals or white powder. Corked bottle.

Solubility 1 part in 10-11 parts water.

Used as hardening agent (page 274), also in hypo-alum toning. (See Jacobson; "Enlarging.")

ALUM, CHROME. Chromium potassium sulphate.  $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ . ANSI PH 4. 151 (1958).

Deep violet crystals.

Soluble 1 part in 5-7 parts water.

Used as hardening agent in hardening fixing baths (page 274).

AMIDOL. 2,4-Diamino-phenol hydrochloride.  $\text{C}_6\text{H}_3(\text{OH})(\text{NH}_2)_2 \cdot \text{HCl}$ . ANSI PH 4. 127 (1965).

White to greyish needle crystals.

WS. 25 parts. SSS. 28 parts. SSC. 26 parts.

Strong developer without alkali (page 198).

**AMMONIA.** Liquid ammonia.  $\text{NH}_4\text{OH}$ .

Colourless solution of ammonia gas in water, with penetrating smell.  
.880 ammonia contains 35%  $\text{NH}_3$ . .910 ammonia contains 25%  $\text{NH}_3$ .  
Corrosive and poisonous.

Used in reversal developers (page 244), and as blackening agent in intensifying (page 348).

**AMMONIUM CARBONATE.** Lump ammonia.  $(\text{NH}_4)_2\text{CO}_3$ .

White lumps or powder, ammoniacal smell. Keep in glass-stoppered bottle.

Soluble 1 part in 4 parts water.

Used in special developers.

**AMMONIUM CHLORIDE.** Sal ammoniac.  $\text{NH}_4\text{Cl}$ . ANSI PH4. 183 (1961).

White crystalline powder.

Soluble 1 part in 3 of water.

Used in preparing quick fixing baths (page 266).

**AMMONIUM BIFLUORIDE.** Acid ammonium fluoride.  $\text{NH}_4\text{F.HF}$ .

White powder. Attacks the skin, poisonous.

Easily soluble in water.

Used for removing gelatine emulsion film from glass plates (page 392).

**AMMONIUM PERSULPHATE.**  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

Colourless crystals.

Soluble 1 part in 1.7 parts of water.

As reducer (page 344).

**AMMONIUM THIOCYANATE.** Ammonium Sulphocyanide.  $\text{NH}_4\text{CNS}$   
BS 3750: 1964.

White deliquescent crystals.

Very soluble in water.

As a rapid fixing agent (page 276).

**AMMONIUM THIOSULPHATE.** Ammonium Hyposulphate.  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ .  
BS 3310: 1960; ANSI PH4. 252 (1960).

White crystals.

Very soluble in water.

As a rapid fixing agent (page 276).

**BENZOTRIAZOLE.**  $\text{C}_6\text{H}_5\text{N}_3$ . BS 3309: 1960; ANSI PH4. 204 (1962).

White crystals.

Insoluble in water.

Antigofgant (page 92).

**BORAX.** Sodium baborate.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . BS 3311: 1961; ANSI PH4.  
230 (1961).

White powder or crystals.

Soluble 1 part in 17 water.

As mild alkali in fine-grain developers (page 204).

**BORIC ACID.** Boracic acid.  $\text{H}_3\text{BO}_3$ . ANSI PH4. 103 (1958).

White lamellar crystals, greasy feel.

Solubility 1 in 25 water.

As addition to fine-grain developers (page 206).

**CALGON.** Presumably sodium hexa-metaphosphate.

White powder or colourless crystals.

To prevent precipitation of calcium salts in hard water.

**COPPER SULPHATE.** Blue vitriol.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . ANSI PH4. 180 (1958).

Blue crystals, poisonous.

Soluble 1 part in 3 water.

As bleach bath (page 345), and as intensifier (page 351).

**CHLORQUINOL.** Mono-chlor-hydroquinone, Adurol.  $\text{ClC}_6\text{H}_3(\text{OH})_2$  ANSI  
PH4. 134 (1964).

Greyish crystalline powder.

Very soluble in water.

Used as developer (page 195).

**CITRIC ACID.**  $C_6H_8O_7 \cdot H_2O$ . ANSI PH4. 102 (1958).  
 Colourless crystals.  
 Soluble 1 part in 0.75 water.  
 In physical developers (page 218).

**FORMALIN.** Solution of gaseous formaldehyde in water.  $H \cdot CHO$  37% w/v.  
 ANSI PH4. 152 (1958).  
 Water clear but faintly yellowish solution, poisonous with unpleasant smell. Vapour dangerous to light-sensitive material.  
 Miscible in all proportions with water.  
 As hardening agent when diluted with water (page 406).

**GLYCERINE.** Glycerol.  $C_3H_5(OH)_3$ .  
 Colourless thick fluid.  
 Miscible in all proportions with water.  
 As softening agent and in enlarging scratched negatives. (See *Jacobson*; "Enlarging.")

**GLYCIN.** p-hydroxyphenyl glycine.  $C_6H_4OH \cdot NH \cdot CH_2 \cdot COOH$ .  
 White crystals.  
 WS. 0.23. SSS. only traces. SSC.  $12\frac{1}{2}$  parts.  
 Slow and very clean-working developer (page 196).

**HYDROCHLORIC ACID.**  $HCl$ . ANSI PH4. 104 (1958).  
 Colourless when pure, but often yellowish. Corrosive and poisonous.  
 Vapour dangerous to photographic materials.  
 In Chromium Intensifier (page 351), also for cleaning dirty vessels.

**HYDROQUINONE.** p-dihydroxybenzene.  $C_6H_4(OH)_2$ . BS 3103:  
 1959; ANSI PH4. 126 (1962).  
 Colourless crystals.  
 WS.  $5\frac{1}{2}$ -6. SSS. 4. SSC.  $7\frac{1}{2}$ .  
 Widely used developer (page 172).

**IRON ALUM.** Ferric ammonium sulphate.  $Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$ .  
 Pale Violet crystals.  
 Soluble 1 part in 7 water.

**IRON CHLORIDE.** Ferric chloride.  $FeCl_3 \cdot 6H_2O$ .  
 Yellow masses.  
 Very soluble in water 1 in 0.6.  
 Used in Belitzki's reducer (page 343).

**MERCURY CHLORIDE.** Mercuric chloride. Corrosive sublimate.  $HgCl_2$ .  
 White crystals. Violent poison.  
 Soluble 1 in 16 water.  
 Used in mercury intensifier (page 348).

**MERITOL** understood to be paraphenylenediamine pyrocatecholate  
 $C_6H_4(NH_2)_2 \cdot C_6H_4(OH)_2$ .  
 Cream or greyish crystalline substance.  
 Used in fine-grain developers (page 211).

**METOL.** Methyl para-aminophenol sulphate,  $C_6H_4(OH)(NH \cdot CH_3)\frac{1}{2}H_2SO_4$ .  
 Colourless needles or prisms.  
 WS. 5. SSS. 2. SSC.  $4\frac{1}{2}$ .  
 Developer of universal applicability (page 172).

**ORTHOPHENYLENEDIAMINE** o-phenylenediamine. 1,2-Diaminobenzene.  $C_6H_4(NH_2)_2$ .  
 White crystals. More stable than paraphenylenediamine.  
 For fine-grain developers (page 210).

**PARA-AMINOPHENOL HYDROCHLORIDE.** p-aminophenol.  $C_6H_4 \cdot (NH_2)(OH) \cdot HCl$ . ANSI PH4. 129 (1954).  
 Colourless crystals.  
 WS. 33. SSS. -. SSC. 3.  
 Rapid developer in caustic alkali solution (page 196). Basis of many commercial concentrated developers.

**PARA-PHENYLENEDIAMINE** 1,4-Diaminobenzene.  $C_6H_4(NH_2)_2$ . ANSI PH4. 132 (1964).

White to brownish powder. Poisonous.

Used in fine-grain developers (p. 210).

**PHENIDONE** 1-phenyl-3-pyrazolidone.  $C_9H_{10}N_2O$ . BS 3230: 1960; ANSI PH4. 136 (1960).

Colourless crystals.

Slightly soluble in water, readily in aqueous acids and alkalis.

Developing agent (page 198).

**POTASSIUM BROMIDE**. KBr. BS 3307: 1960; ANSI PH4. 200 (1962).

White cubic crystals or white powder.

Soluble 1 in 1.6 water.

Restrainer in developers (page 91), also in bleaching baths.

**POTASSIUM CARBONATE**. Potash.  $K_2CO_3$ . BS 3751: 1964; ANSI PH4. 229 (1962).

White powder, attracts moisture with avidity.

Soluble 1 in 1 water.

Alkali for developers (page 85), and as quick-drying medium.

**POTASSIUM DICHROMATE**. Bichromate of potash.  $K_2Cr_2O_7$ . ANSI PH4. 300 (1958).

Orange red crystals, poisonous.

Soluble 1 part in 10 water.

For cleaning vessels (page 391).

**POTASSIUM FERRICYANIDE**. Red prussiate of potash.  $K_3Fe(CN)_6$ . BS 3752: 1964; ANSI PH4. 302 (1958).

Dark red crystals, poisonous.

Soluble 1 in 2.5 water.

As reducer (page 342), and in bleach baths (page 373).

**POTASSIUM HYDROXIDE**. Caustic potash. KOH. BS 3753: 1964; ANSI PH4. 326 (1956).

Appears in sticks, flakes and pellets, strongly corrosive and attracts moisture.

Extremely soluble in water, 1 in 0.5.

Strong alkali for developers (page 86).

**POTASSIUM IODIDE**. KI. ANSI PH4. 201 (1957).

White cubic crystals.

Soluble 1 in 0.7 water.

As addition to developer (page 379), and for intensifier (page 350).

**POTASSIUM METABISULPHITE**.  $K_2S_2O_5$ . BS 3306: 1960; ANSI PH4. 277 (1957).

Colourless, hard crystals.

Soluble 1 in 3 water.

As preservative in developers (page 83), stop bath (page 271), as acidifier in fixing baths (page 264), as clearing bath (page 247).

**POTASSIUM PERMANGANATE**.  $KMnO_4$ . ANSI PH4. 301 (1958).

Glistening violet black crystals.

Soluble 1 in 16 water.

As reducer (page 343), hypo test (page 291).

**POTASSIUM THIOCYANATE**. Potassium sulphocyanide. KCNS. BS 3833. 1965.

Colourless crystals, poisonous.

Soluble 1 in 0.5 water.

Addition to fine-grain developers (page 203), rapid fixing agent (page 276).

**PYROCATECHIN**. catechol. Orthodioxxybenzene.  $C_6H_4(OH)_2$ .

White crystals.

Developer (page 194).

WS. 33. SSS. -. SSC. 36.

**PYROGALLOL.** Pyro. Pyrogalllic acid. Trioxybenzene.  $C_6H_3(OH)_3$ . ANSI PH4. 130 (1956).

Colourless crystals, poisonous.

WS. 52. SSS. 59. SSC. 42.

Developer (page 196).

**SILVER NITRATE.**  $AgNO_3$ .

Colourless crystals, poisonous and strong caustic.

Soluble 1 in 1 water.

Physical development (page 219), intensification (page 351).

**SODIUM BISULPHITE.**  $NaHSO_3$ .

Does not exist as a solid although listed in some catalogues. Sodium or potassium metabisulphites are used, which on dissolving in water give a solution of the bisulphite.

Soluble 1 in 4 water.

Used for same purposes as potassium metabisulphite.

**SODIUM BISULPHITE LYE.** Average density  $36^\circ$  Baume = 1.33 sp. G.

Colourless or pale yellow fluid. Glass bottle with rubber stopper.

Used for same purpose as sodium bisulphite (see above).

**SODIUM CARBONATE.** Soda. Carbonate of soda.  $Na_2CO_3$  and  $Na_2CO_3 \cdot 10H_2O$ . BS 3305: 1960; ANSI PH4. 228 (1961) and PH. 4227 (1961).

White crystals or powder. Crystal carbonate.

Soluble 1 in 1.6 water, anhydrous 1 part in 6 water.

Used as alkali in developers.

**SODIUM CHLORIDE.** Common salt.  $NaCl$ . ANSI PH4. 203 (1956).

White powder.

Soluble 1 in 2.5 water.

Addition to mercury intensifier and copper bleach bath (page 345).

**SODIUM HYDROXIDE.** Caustic soda.  $NaOH$ . BS 3308: 1960; ANSI PH4. 225 (1960).

In sticks, flakes and pellets, strong caustic.

Soluble 1 in 1.7 water. (Generates heat on dissolving as does caustic potash.)

Strong alkali for developers (page 86).

**SODIUM PHOSPHATE, TRIBASIC.**  $Na_3PO_4 \cdot 12H_2O$ .

White crystals.

Soluble 1 in 5 water.

As alkali in developers (page 379).

**SODIUM SULPHATE.** Glauber's salts.  $Na_2SO_4 \cdot 10H_2O$ .

Colourless crystals.

Soluble 1 in 2 water.

As addition to tropical developer (page 228).

**SODIUM SULPHIDE.**  $Na_2S \cdot 9H_2O$ .

Colourless crystals, somewhat corrosive.

Very soluble in water.

Used in intensifying and toning (see *Jacobson*; "Enlarging.")

**SODIUM SULPHITE.**  $Na_2SO_3 \cdot 7H_2O$ . BS 3303: 1960.

White powder or crystals.

Anhydrous salt soluble 1 in 5 water.

Preservative in developers (page 81), as blackening agent (page 348).

**SODIUM THIOSULPHATE.** Hypo. Sodium hyposulphite.  $Na_2S_2O_3 \cdot 5H_2O$ . BS 3301: 1960; ANSI PH4. 251 (1960).

Colourless crystals or powder (anhydrous).

Soluble 1 in 0.7 water.

The universal fixing—agent (page 263).

**SULPHURIC ACID.**  $\text{H}_2\text{SO}_4$ . ANSI PH4. 101 (1958).

Colourless oily liquid. Strong corrosive and poisonous.

*Caution:* When dilute acid is required, the acid must always be poured into the water, never the reverse, otherwise the reaction attains explosive violence.

Used in bleach baths (page 345), cleaning solution (page 401).

**URANIUM NITRATE.** Uranyl nitrate.  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

Yellowish crystals. Poisonous.

Soluble 1 in 0.5 water.

Used in uranium intensifier (page 350).

## *Recommended Further Reading*

- Attridge, G.G. and Walls, H. J., *Basic Photo Science*, Focal Press, London (1977).
- Baines, H., *The Science of Photography*, Fountain Press, London (1967).
- Eaton, G. T., *Photographic Chemistry*, Morgan and Morgan, New York (1963).
- Focal Encyclopedia of Photography*—Desk Edition, Focal Press, London (1969).
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